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On substituting air, the cyanogen exerted finally a pressure of 740 millim. This would appear to indicate that palladium is quite impermeable to cyanogen, and is not attacked by it at 280°.

Experiment 22.—Nitric oxide was introduced into the tube, at a barometric pressure (corrected) of 765 millim. On passing hydrogen the pressure rose 368 millim.; the total pressure of the gases in the tube was $368 + 763 = 1131$ millim., the barometric height being 763 millim. The increase of pressure was therefore $1131 - 765 = 366$ millim. Supposing that the nitric oxide had reacted with the hydrogen, forming nitrogen and water, thus :—



the pressure of the nitric oxide would have been halved, and would have amounted to $765/2 = 382.5$ millim. But it is to be supposed that the resulting water would have exerted its usual vapour-pressure; and as its temperature was 22°, the pressure of the water-vapour would be 18.5 millim.

We have thus :—

			millim.
Pressure of $\text{H}_2 + \text{N}_2 + \text{H}_2\text{O}$ vapour .	368	+ 763	= 1131
Pressure of $\text{N}_2 + \text{H}_2\text{O}$ vapour .	382.5	+ 18.5	= 401

$$\text{Hence pressure of hydrogen alone} = 730$$

and the quotient $730/765 = 0.9543$, a number almost identical with those previously obtained.

Experiment 23.—A similar experiment was made with nitrous oxide. Here, too, reduction occurs at 280°; but the volume of the residual nitrogen is equal to that of the nitrous oxide.

The initial pressure of the nitrous oxide was 772 millim. After passing hydrogen, the total pressure was 1489.5 millim. The difference, 717.5 millim., is to be ascribed to hydrogen and water-vapour. The barometer stood at 761 millim. Deducting 18.5 millim., the pressure of water-vapour at 22°, the pressure of the hydrogen alone is 699 millim. And the quotient $699.0/761 = 0.9186$.

The hydrogen was then removed by a current of air on the

external surface of the palladium. The pressure of the nitrogen was then 780·5 millim. Again restoring hydrogen on the exterior, the pressure rose to 727·5 millim., the barometric pressure being 761 millim. The pressure ascribable to hydrogen and water-vapour is thus 708 millim.; subtracting the pressure of water-vapour, 22·5 millim., the remainder, 685·5 millim., is due to hydrogen. The quotient is 0·9008. Here again a reasonable correspondence is found.

It is evident that in all cases the pressure of the hydrogen in the interior of the palladium tube is lower than the barometric pressure, *i. e.* lower than the pressure of the hydrogen on the exterior. It will be convenient here to tabulate the ratios found :—

a. Mean ratio from hydrogen and nitrogen at 280° .	0·9053
b. Ratio at 335°	0·8984
c. Ratio with 50 per cent. of hydrogen at 335° . .	0·9362
d. Ratio with 25 per cent. of hydrogen at 335° . .	0·9344
e. Ratio from hydrogen and carbon dioxide at 280° .	0·9621
f. Ratio from hydrogen and carbon monoxide at 280° .	0·9545
g. Ratio from hydrogen and cyanogen at 280° . .	0·9693

I omit the two last determinations, as uncertainty was introduced owing to the presence of water-vapour.

On reviewing these results, it would appear that the ratio is not altered by rise of temperature above 280°. The same number was obtained at 280° and at 335°. But at a lower temperature the ratio is much smaller, if, indeed, the end-point was really reached. Dilution of the hydrogen appears to raise the ratio; and the presence of carbon dioxide, carbon monoxide, or cyanogen in the interior of the palladium tube appears to be favourable to the passage of hydrogen.

To what are these results to be ascribed?

Troost and Hautefeuille have determined the pressures of dissociation of the definite hydride of palladium, Pd_2H (*Compt. rend.* lxxviii. p. 686). At 130° the pressure is nearly equal to that of the atmosphere, it is 624 millim.; while at 140° the pressure is 812 millim. It rises rapidly with temperature, and at the highest temperature given, 170°, it amounts to the large number 1840 millim. It is impossible to believe, then, that any hydride of palladium should exist even at the lowest of

the temperatures employed, 223° . Yet palladium becomes quickly permeable to hydrogen only at a higher temperature.

Two questions require answer :—(1) Why is palladium permeable to hydrogen? and (2) Why is the pressure of the internal hydrogen always less than that of the external hydrogen?

(1) It is hardly probable that the palladium acts simply as a filter, allowing small molecules of hydrogen to pass while blocking the passage of larger molecules of other gases. Graham, however, appears to regard this as in some measure the cause of the passage. His words are :—“ Such phenomena of gaseous penetration appear to suggest a progression in the degree of porosity. There appear to be (1) pores through which gases pass under pressure or by capillary transpiration, as in dry wood and many minerals ; (2) pores through which gases do not pass under pressure, but pass by their proper molecular movement of diffusion as in artificial graphite ; and (3) pores through which gases pass neither by capillary transpiration nor by their proper diffusive movement, but only after liquefaction, such as the pores of wrought metals and the finest pores of graphite.”

It is noteworthy that Graham considers that gases are liquefied in the pores of metals. But in the experiments here described this can hardly be the case. For at 270° and at higher temperatures hydrides of palladium do not exist, as is conclusively shown by Troost and Hautefeuille ; just as water does not exist in superheated steam. And yet it is at these temperatures that palladium is permeable to hydrogen, and not at temperatures at which hydride of palladium is stable.

There are several facts which must be borne in mind in seeking for an interpretation for the phenomenon of the passage of hydrogen through palladium.

First. The hydrogen in the act of passing is a reducing agent, as shown by its behaviour towards the oxides of nitrogen. At such temperatures as were here employed, hydrogen is without action on the lower oxides of nitrogen.

Second. Bellati and Lussano have shown (*Atti R. Ist. Ven.* i. series vii. p. 1173) that hydrogen “diffuses” through an iron plate which is used as a negative electrode on electrolysing dilute sulphuric acid. Their observation has been

confirmed and amplified by Shields (Chem. News, lxx. p. 195). Shields has shown that neither lead nor platinum nor palladium allow hydrogen to pass under similar circumstances, and experiments made by myself show that nickel does not allow carbon monoxide to pass at temperatures at which that compound is stable.

Third. Iron and platinum, as shown by Deville and Debray (*Compt. rend.* lvii. p. 965), are permeable at a red heat to hydrogen.

I think these considerations prove that it is necessary to add a fourth class to the three classes suggested by Graham. Graham's first class involves actual holes, that is, passages large in comparison with the molecular diameter; his second implies pores small compared with molecular diameter, but still greatly exceeding that diameter; his third class would be termed "solid solution" in the present state of our knowledge, *i. e.* when coal-gas passes through india-rubber, the latter dissolves the gas on the side exposed to it, while the gas evaporates from the other side, so as to render the pressure of the dissolved gas equal on both sides of the membrane. The case is precisely analogous to the passage of water through a semi-permeable diaphragm. But, in order that hydrogen may pass through iron, it must be in the state in which it is liberated by an electric current, or it must be hot. That hydrogen will not pass through palladium at the ordinary temperature appears to show that the compound of palladium and hydrogen has practically no dissociation pressure at ordinary temperature; otherwise the hydrogen would pass by solution, in the same manner as coal-gas passes through india-rubber, or water through a semi-permeable diaphragm. That it will not pass, even when liberated by an electric current on one side of the palladium membrane, shows that it at once enters into combination with the palladium, and is no longer *in statu nascendi*, to use a generally understood expression which is independent of theory. But that it passes through hot palladium appears to show that it is then in a state analogous to that of electrically liberated hydrogen.

It is known that electrified bodies are discharged if a flame burns in their vicinity. This may be attributed to the liberation of atomic oxygen in a kind of Grotthus chain. For

it may be imagined that when a molecule of oxygen encounters the oxidizable matter of a flame, it is dissociated : while one atom serves to oxidize the carbon, the other exchanges with a neighbouring molecule, and a succession of exchanges occur till the atomic oxygen near the electrified body receives or communicates a charge, and restores the potential of the charged body to that of surrounding objects.

To ascertain whether a flame of oxygen burning in hydrogen would similarly cause the hydrogen to assume the atomic state, a piece of apparatus was contrived in which such a flame burned in close proximity to a very thin iron plate, on the other side of which a Torricellian vacuum was maintained. No hydrogen passed through the plate : hence either the hydrogen was not atomically transferred, as oxygen is supposed to be under similar circumstances, or such atoms were unable to pass through the plate as they would have done if liberated electrically. It must be noticed, however, that it is conceivable that the double atom of hydrogen which we term a molecule may have united directly with the oxygen, without separating into its two components. The result of this experiment is therefore inconclusive.

It appears to me necessary to suppose that at a temperature far above that at which hydride of palladium is capable of existence, the palladium has still the power of so attracting the hydrogen that the molecule is split. This necessarily implies a gain of energy, so far as the splitting of the hydrogen molecule is concerned, for any energy lost by the temporary and transient union of hydrogen and palladium is at once gained during its escape on the other side of the partition. But the hydrogen in expanding, which it does on passing through the partition, loses energy, and hence, on the whole, energy will probably be lost during the process. It is to such theories, I think, that we must look to explain the passage of hydrogen through a palladium diaphragm.

(2) In answering the question why the pressure raised by the entering hydrogen is never equal to that of the atmosphere, I think it must be admitted that the gas contained in the palladium vessel is not without influence on the passage of the hydrogen. A diminution of the pressure of the external hydrogen by the addition of nitrogen considerably increases

the partial pressure of the internal hydrogen. Here the action of external nitrogen apparently neutralizes partially the effect of the internal nitrogen, and more hydrogen penetrates the metallic diaphragm. With gases other than nitrogen in the interior, the pressure of the hydrogen becomes more nearly equal to that on the exterior. The constancy of the results, however, proves that the deficiency is not due to experimental error.

This whole subject is full of difficulty. Experiments are in progress on the absorption of gases by platinum, and on the passage of gases through other metallic diaphragms, which may ultimately render an explanation possible. But I have thought it desirable to place these experiments on record, incomplete as they are, rather than wait for a complete solution to the problem.

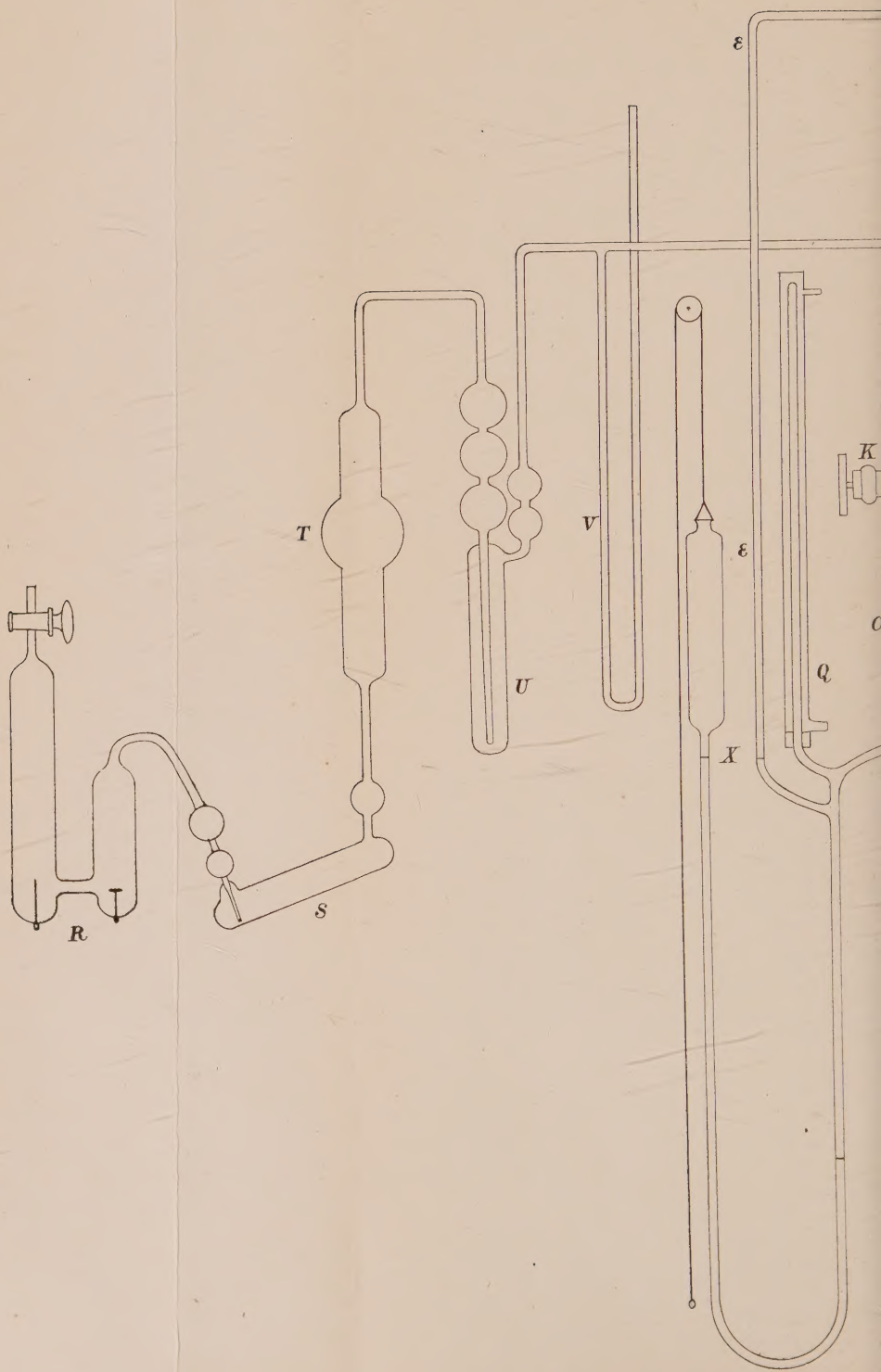
I cannot conclude without acknowledging the able manner in which my late assistant, Mr. Percy Williams, has aided me in carrying out these experiments.

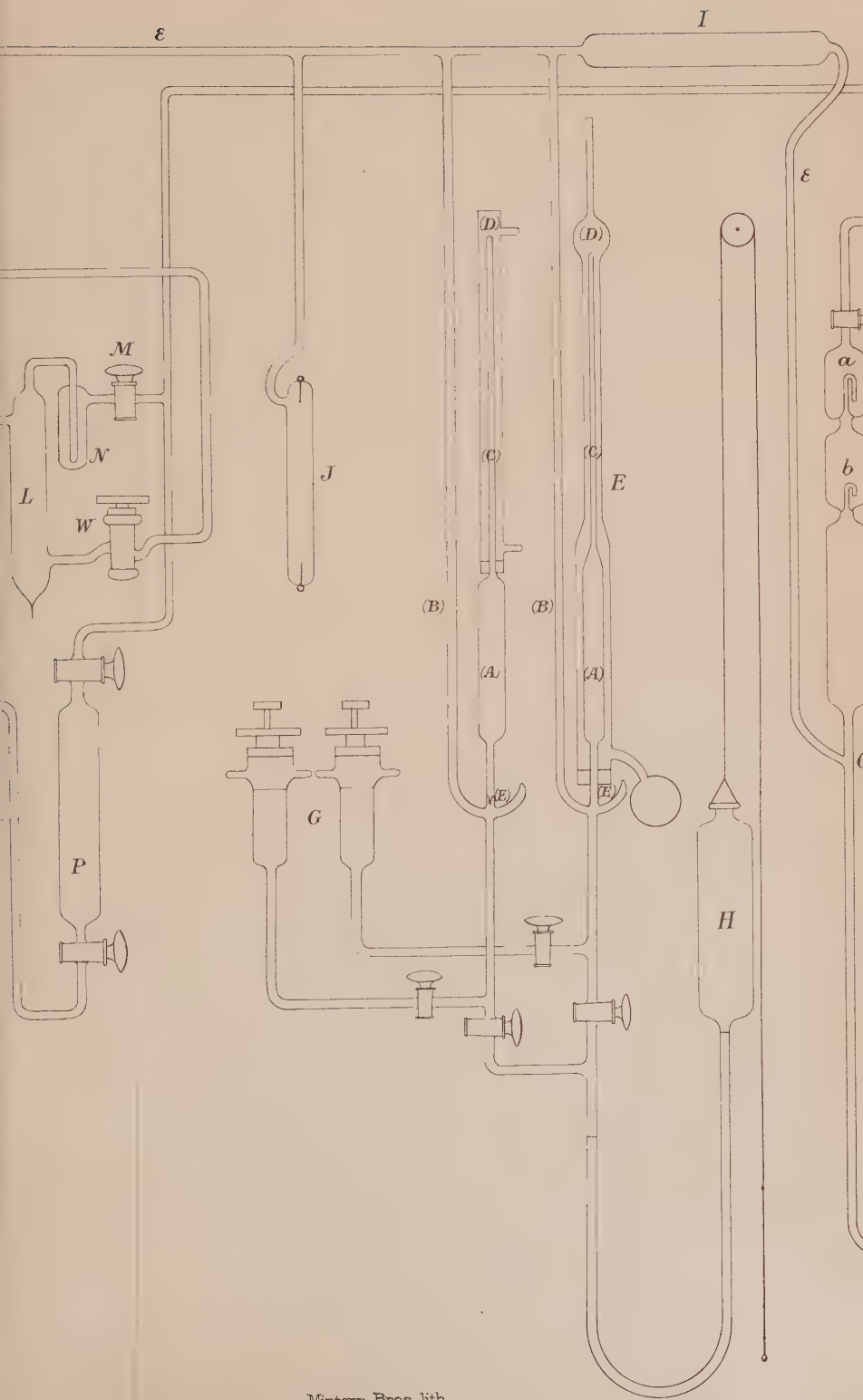
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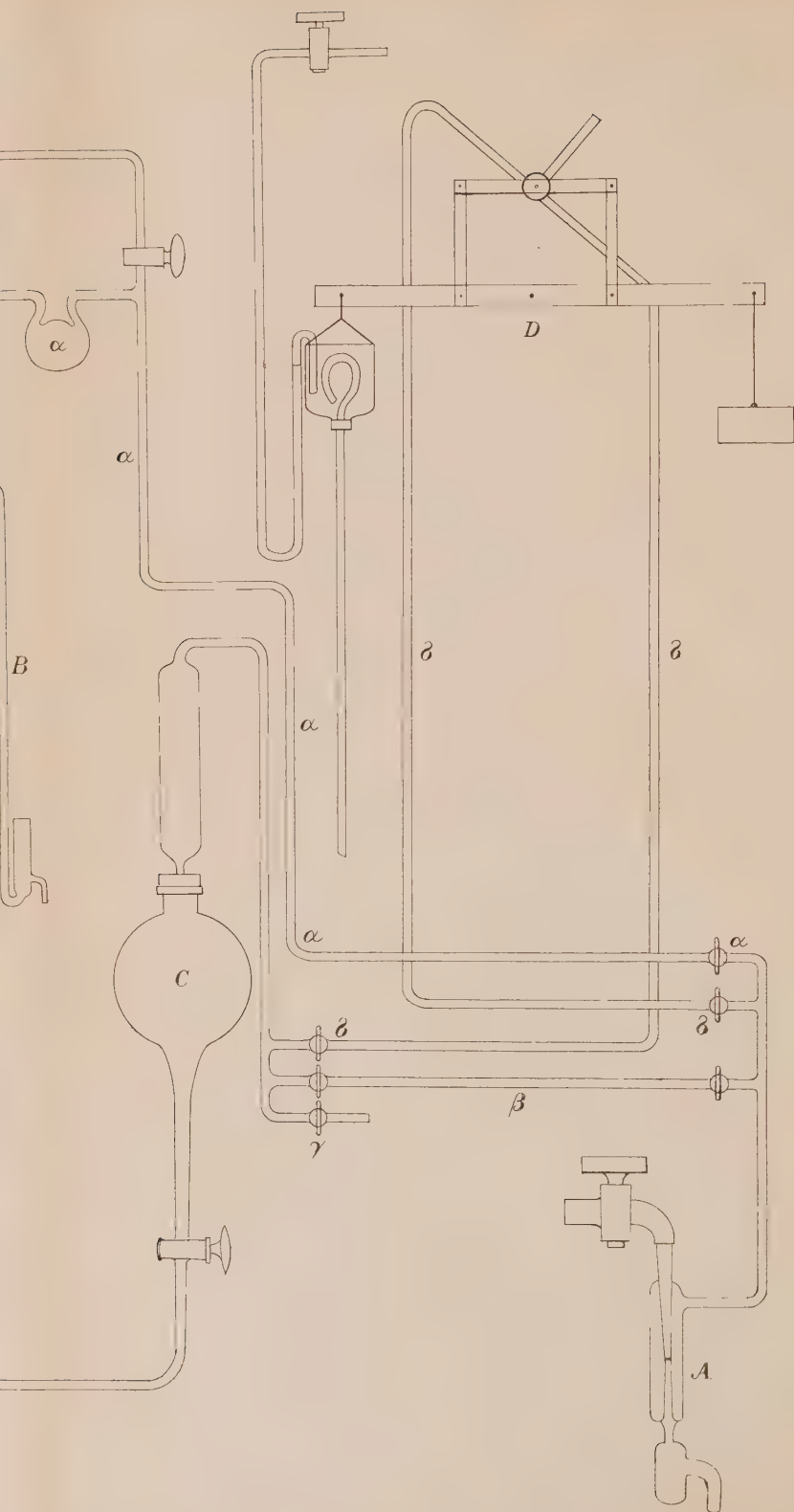
Mr. MOND thought the fact that rise of temperature accelerates diffusion tended to confirm Graham's view that the gases pass through openings in the solid, for increase of temperature would widen any pores which might exist in the metal.

The PRESIDENT enquired whether the author's argument against the possibility of palladium hydride condensing in the pores of the metal, because of its being unstable at the temperature employed, would be affected by the fact of water being capable of existing in contact with glass at temperatures much above boiling-point.

In reply Prof. RAMSAY said the President's suggestion might be true, but if so another condition must be fulfilled, viz., that the hydrogen molecules must be split up into the atomic or *nascent* state.







XIX. *Experiments on the Relations of Pressure, Volume, and Temperature of Rarefied Gases.* By E. C. C. BALY, 1851 Exhibition-Scholar in University College, London, and WILLIAM RAMSAY, Ph.D., F.R.S.*

[Plate VII.]

THE experiments of which we give an account in the following pages are of two kinds:—first, they relate to the trustworthiness of measurements by means of the McLeod gauge; and second, they deal with the thermal expansion of gases at low pressures. The behaviour of the ingenious gauge invented by Professor Herbert McLeod has, so far as we know, not been carefully investigated. The thermal expansion of gases at low pressures has been the subject of two investigations, one by Mendeléeff, and one by G. Melander. But many researches have been made on the relations of volume to pressure at constant temperatures; and as there is an intimate connexion between the compressibility of gases and their thermal expansion, we think it desirable to give a short summary of the work which has already been done on the subject. It is obvious that if the product of pressure and volume of a gas diminishes with the degree of rarefaction, it is to be expected that its coefficient of expansion with rise of temperature will increase; whereas, if the p_v increases as observed by Mendeléeff and others, its coefficient of expansion will probably diminish.

HISTORICAL RÉSUMÉ.

1. *Relation of Volume to Pressure at Constant Temperature.*

For more than twenty years the question of the validity of Boyle's Law, applied to rarefied gases, has been the subject of frequent articles in scientific journals. In 1873 Siljeström (*Bihang till K. Svenska Vet. Akad. Handlingar*, ii. p. 1) published in Swedish an account of experiments to test this important law. His method consisted in exhausting one of two stout cylindrical metal vessels connected together by

* Read May 25, 1894.

means of a tube provided with an air-tight stopcock. Both vessels were placed in a large reservoir of melting ice in order to maintain temperature constant at 0° . Each vessel was provided with a mercury manometer; and while the larger of the two had no opening except the tube already mentioned, which connected it with the smaller vessel, the latter was joined by means of a brass tube with a stopcock to an ordinary exhausting air-pump, also furnished with a mercury gauge.

The plan of operation was as follows:—The pressure of gas in the smaller vessel was reduced by means of the air-pump, communication with the larger vessel being cut off by means of the stopcock, and the pressure of the gas in both vessels was read on the mercury gauges attached to them, and also on that attached to the air-pump. The pressure registered by the gauge of the smaller vessel and by the air-pump gauge should of course be the same. Communication with the air-pump was then shut off. The stopcock between the two vessels was then opened, and gas passed from the larger to the smaller. After time had been allowed for equilibrium of temperature and pressure to be re-established, the pressures on the gauges were again read. The capacities of the vessels being accurately known, the product of pressure and volume could be calculated.

Sixteen series of experiments, each consisting of fourteen individual readings, were made with air; the diminution of pressure varied in these series from that of the atmosphere to 1.4 millim.; and by means of an accurate cathetometer the pressure was read to the second decimal place. The ratio of V (the volume of the closed reservoir) to $V + V'$ (that of both reservoirs) was calculated by means of the formula

$$E' = \frac{E(V + n\mu)}{V + V' + n'\mu} = \frac{eV'}{V + V' + n'\mu},$$

where

E is the original pressure of the gas;

e , pressure read on gauge of second cylinder or of air-pump after exhausting;

E' , pressure in cylinders after opening the stopcock;

$n\mu$ and $n'\mu$, small corrections introduced, due to alteration

in total volume of apparatus owing to rise of mercury in the gauges. n is a number of centimetres, μ the capacity of one centim. of the gauge.

β (in following equation) = μ/V . Hence

$$\frac{V'}{V} = \frac{E(1+n\beta) - E'(1+n'\beta)}{E' - e}.$$

If the ratio $(V + V')/V$ remains constant, Boyle's law holds ; if, on the contrary, $(V + V')/V$ be too great or too small, the pressure E' would be either less or greater than corresponds with Boyle's law.

The results were averaged, series a and b being compared with series c and d ; the latter with series e and f , and so on. This process yielded six sets of average values of $(V + V')/V$ for air. The results follow :—

Extremes of pressure.				$V + V'/V$.
759	and	352	millim.	. . 1.47209
352	„	164	„	. . 1.47165
164	„	77	„	. . 1.46887
77	„	37	„	. . 1.46870
37	„	18	„	. . 1.46122
18	„	7	„	. . 1.46511

These values of $V + V'/V$ decrease with falling pressure ; the higher its value the lower the value of E' , and *vice versa*. Assuming from Regnault's observations between 1 and 30 atmospheres that at a pressure of 1 atmosphere the value given above, 1.47209, is correct, and that Boyle's law holds under such a pressure, it follows that the pv of the air increases with decreased pressure. This conclusion, too, Siljeström considers to be rendered probable by Regnault's own work. For he, too, found that air is up to a certain degree more compressible at pressures higher than that of the atmosphere. For example, if Regnault's results for pressures between 3 and 6, between 6 and 12, and between 12 and 24 atmospheres be termed k' , k'' , and k''' respectively, then

$$k''/k' = 0.997128 ; \quad k'''/k'' = 0.999386.$$

The question of course is, Can these and similar ratios increase to above unity ?

Siljeström found from similar but less numerous experiments with oxygen and with carbon dioxide that the variation in the ratio $(V + V')/V$ was in the same direction. His results with hydrogen are :—1·47247 at 759–351 millim. ; 1·47302 at 351–162 millim. ; 1·47258 at 162–75 millim. ; and 1·46895 at 75–17 millim.

Siljeström's results are criticised by Mendeléeff and by Amagat. Any error which he might have made is cumulative, as pointed out by Van der Ven, whose work will be subsequently considered.

Mendeléeff's work is at present unfinished, or at least a description of it in full has not yet appeared. His main work appeared in Russian in 1875, and the first part consists of 267 pages folio ; the second part is not yet published. We owe to the kindness of Dr. Jas. Walker an account of the contents of this large volume. Short accounts of Mendeléeff's general conclusions are to be found in French in the *Mélanges Physiques et Chimiques tirés du Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg*, ix. ; also *Annales de Chimie et Physique*, [3] ix. 1876. These abstracts leave much to be desired.

Mendeléeff states that he tried nearly a dozen different forms of apparatus before a satisfactory one was devised. This, he says, is figured in volume ii. table 15 (unpublished)* ; but he gives the following description of it in a lecture delivered before the Imperial Russian Technical Society in January 1881. It consisted of an ovoid glass vessel, with a capacity of about $3\frac{1}{2}$ litres, placed in a trough of water. The lower portion of this vessel terminated in a tube, one metre in length, provided at its lower end with a stopcock ; the volume of air was determined by weighing the mercury run out from this vessel. A tube was sealed to this vertical tube, which served to fill the measuring-vessel with mercury when required. A capillary tube was attached to the upper part of the measuring-vessel ; it communicated with two lateral descending tubes, through one of which gas could be introduced at will. It was closed by raising a reservoir of mercury, and covering an opening more than thirty inches below the

* Professor Mendeléeff informs us that a large part of the second volume is now in manuscript.

top of the measuring-vessel; but when the reservoir was lowered, gas could be passed into the measuring-vessel, through the capillary tube. The second descending tube connected the measuring-vessel with a wide manometer, formed like a siphon; and by means of a reservoir it was possible to raise the mercury in the open limb to a mark with great accuracy. Corrections were introduced for temperature, measured by a differential air-thermometer, and also for the varying volume of the apparatus due to the different heights of the mercury in the manometer. It is easy to see how this apparatus could be employed to test Boyle's law. To test Gay-Lussac's, he describes the operation thus:—

“The mercury is run out of the measuring-vessel to a mark on the capillary tube, and weighed. Let this be done at the temperature of boiling water. Now cool the bath to 0° by surrounding the vessel with ice—the pressure begins to diminish as is indicated by the manometer; but we will not allow it to do so. By means of the stopcock and the other capillary, we let mercury run into the vessel until the pressure of the gas at 0° becomes the same as it was at 100° . The apparatus is then raised to the ordinary temperature, and the mercury which entered the tube at 0° is run out and weighed. This weight and the previous one give us the data necessary for calculating the true coefficient of expansion of gases.”

No final numbers are given in Mendeléeff's published papers, so far as we have been able to discover; but the general result is stated thus:—

The product of pressure into volume, pv , which according to Boyle's law should be constant, varies considerably with diminution of pressure; at low pressures pv/dp is positive, *i. e.* the gas is less compressible than it would be if it followed Boyle's law. Stating the case broadly, it may be said that at low pressures gases approach the state of a liquid or a solid; or pv increases with decrease of p ; or e/d increases, for $d=1/v$.

We have thought it advisable to give a tolerably full description of Siljeström's and Mendeléeff's experiments, because they are described in languages not generally known; we may discuss the remaining researches on the subject in

much shorter space, seeing that they are described in French and in German.

Amagat, in 1883 (*Annales de Chimie et Physique*, xxviii. p. 480), undertook experiments to test the results obtained by Siljeström and Mendeléeff, but was unable to confirm them. His conclusion is, that for the lowest pressures measured (6.54 millim.) the differences were sometimes positive, sometimes negative ; and that the necessary error of experiment was of an order of magnitude equal to that of the differences found. One of the main difficulties of observation was found in the diffraction of the walls of the manometer in which he measured the pressures to which the gases were exposed. He appears, however, to have been successful in overcoming this difficulty, by the use of polished plane surfaces ; but it is noteworthy that a suspicion of this source of error does not appear to have occurred to either of the former experimenters. Amagat also states that the utmost limit of measurement is probably overestimated at 0.01 millim. ; and indeed it is very difficult, if not impossible, to judge of the contact of two lines, the cross-wire of the cathetometer and the meniscus of the mercury in the gauge, to within such a minute distance. One of his criticisms of Mendeléeff's paper is worth quoting:—

“ In M. Mendeléeff's experiments, a set of values of pv are obtained corresponding to a tolerably limited range of pressures ; this would seem favourable to a knowledge of the direction in which these products alter ; but it is necessary to guard against possible illusion in this matter.

“ A constant cause of error may affect all these products ; for as they deal with smaller and smaller values the effect will be more and more marked, and a regular variation may be conceived to exist, with no foundation in fact. Such an effect would be produced, for example, if the vacuum in the barometer were not absolute. It is certain, that whatever precautions be taken, this vacuum is not absolute ; the effect of this is to diminish the real value of the pressures, that is to say, too small pressures are read : hence the value of p/p' is reduced, and since p is smaller than p' , the values of $pv/p'v'$ are rendered too small ; and as the error increases with reduction of pressure, they will ultimately be less than unity.”

Amagat proceeds to point out that even the vapour-pressure

of mercury ceases to be negligible when a few hundredths of a millimetre cause the supposed deviation.

In 1886, C. Bohr (Wied. *Ann.* xxvii. p. 459) measured the pressures and volumes of rarefied oxygen. His conclusions are that at a temperature of $11^{\circ}4$ oxygen deviates from Boyle's law. For values of pressure greater than 0.7 millim., $(p + 0.109)v = k$; and for lower pressures, $(p + 0.070)v = k$. At 0.7 millim. therefore oxygen undergoes a sudden change and becomes more compressible. This is a very strange conclusion, but it has been confirmed by our work.

In criticising Bohr's work, it is to be noted that he employed very wide tubes, one as barometer, the other to contain the rarefied gas. His method of reading was ingenious. Finding it impossible to read the level of the mercury in such wide tubes with accuracy, he placed in each a glass ball, and read its upper surface. The readings therefore appear to be very accurate. But the shape of the meniscus of mercury is different in a nearly perfect vacuum and in a vessel containing gas; it is always flatter in the vacuous tube. Hence the volume read was probably always too small; and increasingly smaller as the gas was more compressed. This would render the value of the product pv increasingly smaller, and necessitate the correction he applies. It would, however, not explain the breach of continuity which he observed.

Next in order of time comes a paper by F. Fuchs (Wied. *Ann.* xxxv. p. 430) in 1888. The lowest pressure which he measured was 248 millim.; but though he found deviations in the case of sulphur dioxide, hydrogen was normal.

In 1889, E. van der Ven carried out experiments by a method nearly identical with Siljeström's, but avoiding the possibility of cumulative errors which Siljeström's method involved. His conclusion is opposite to that of Mendeléeff and Siljeström; it is:—If a volume of air under low pressure, contained in a closed space, be doubled, it behaves as if its pv decreased with decrease of pressure. Thus he finds

At 62 millim. pressure,	$pv = 0.9873$,
At 31 " "	$pv = 0.9811$,
At 16 " "	$pv = 0.9740$.

Van der Ven used iron cylinders with walls 6 millim. thick,

and it is unlikely that any appreciable alteration in their volume would be caused by the differences in pressure which occur in his experiments. He appears also to have been careful about the temperature of the vessels. But the latter part of his paper is occupied with a discussion of the capillarity of his mercury-gauge; and it appears to us that a possible source of error lies here. For the height of the meniscus of mercury in a gauge is undoubtedly altered by the pressure of the gas in contact with it; and as the gas was rarefied, the apparent difference in height of the mercury in a narrow gauge like the one he employed would be influenced not merely by capillarity, but also by the form of the meniscus. We regard it as probable that the capillarity of mercury, like that of other liquids, is altered by the gas in contact with it. In the empty, or comparatively empty part of the gauge, the capillary depression of the mercury is almost certainly not so great as in that limb exposed to gas; and the alteration of the pressure of the gas doubtless also alters the capillary depression. It would be worth while making this the subject of special experiments.

2. *Expansion of Gases at Constant Pressure, on Rise of Temperature.*

The last paper falling under our notice is one by G. Me-lander, published in 1892 (*Wied. Ann.* xlvii. p. 136). It deals with the thermal expansion of gases under reduced pressure. He concludes that the coefficient of expansion of air decreases from 0.003666 at 752 millim. to 0.0036594 at 232 millim., and again increases, with reduction of pressure, until at 6.6 millim. it amounts to 0.0037627; the turning-point of carbon dioxide is 76.2 millim.; with hydrogen there is no change in direction, but the coefficient increases from 0.0036504 at 764.5 millim. to 0.0037002 at 9.3 millim. These conclusions are opposed to those of Siljeström and Mendeléeff; for if the pv increases, as stated by these authors, it is to be expected that the coefficient of expansion should decrease with decrease of pressure.

Before concluding this historical sketch, we feel it necessary to point out that it is exceedingly unlikely that these

experimenters were dealing with pure gases. It is true that their apparatus were filled with comparatively pure gases ; but they do not seem to have realized the fact that on reduction of pressure, gas different from that with which they were dealing comes off the walls of the containing vessel. When this is of glass, a very considerable amount of carbon dioxide is always evolved. At high pressures, of course, this would make a small difference, probably inappreciable ; but as the pressure becomes lower, a gas like hydrogen will be partly removed, and its place taken by carbonic anhydride. One can never be certain of the purity of the gas measured unless its vacuum-tube spectrum is free from that of other gases.

Another source of error, small in itself, but possibly important when the small deviations which the experimenters are endeavouring to measure are taken into consideration, is of the nature of that pointed out by Lord Rayleigh as applying to Regnault's determination of the comparative weights of hydrogen, oxygen, and nitrogen. It is that the volume of a glass (and presumably of an iron) vessel is considerably diminished if it be partially exhausted, owing to the external pressure of the atmosphere not being balanced by equal pressure in the interior. In Mendeléeff's experiments, for example, in which glass vessels were used, and in which the volume of the gas was ascertained by weighing the mercury run out of the vessel, it appears not unlikely that at low pressures the vessel contained less gas than at high pressures. The values of the products of pressure and volume, p_v , might really remain constant with decrease of pressure ; but as he read pressure directly, and assumed a volume which was probably too great, he registered an increase. We are informed, however, by Professor Mendeléeff, that he introduced a correction for this possible deviation.

All the researches described aim at a direct measurement of pressure. Now there is a limit to the possibility of such measurement, and when the pressure is low, the readings necessarily involve considerable relative error, the extent of which is difficult, if not impossible, to gauge.

We have therefore adopted a different plan, which admits

of the observation of the behaviour of gas at pressures much lower than most of those previously employed. We have met with difficulties, subsequently to be alluded to, which may vitiate the results for some gases ; but for hydrogen the results are fairly trustworthy.

To describe the method in a few lines :—Two McLeod gauges are exhausted in communication with each other : one is heated to a known high temperature ; and at the same instant, both are closed ; after cooling the pressure is read in both. The readings afford data from which the expansion of the gas may be calculated.

DESCRIPTION OF THE APPARATUS.

The apparatus used for these experiments consisted essentially of two McLeod gauges placed side by side on a stand. These gauges were connected on the right to apparatus for exhausting them, and on the left to apparatus for admitting into them, when exhausted, measured quantities of the gas under examination.

The apparatus for exhausting shown on the right-hand side of the diagram (Pl. VII.) consisted of a water-pump A worked by high-pressure water, and capable of giving a vacuum of 11 millim. of mercury.

The exhaustion of the apparatus was commenced by this pump and completed by the mercury-pump B. This mercury-pump discharged the gas taken out at each stroke into a Torricellian vacuum which was sealed by two siphons *a* and *b*. By this means the gas in the large chamber of the pump suffered at most compression up to 4 millim. of mercury, so that the possibility of any considerable condensation of gas on the glass walls was eliminated, and each stroke of the pump removed as nearly as possible the theoretical quantity of gas.

For the preliminary exhaustion of the apparatus the water-pump A was connected with the top of the mercury-pump through the tubes and drying apparatus *αα*. When this preliminary exhaustion was complete, the mercury-pump was brought into action. The lowering and the raising of the mercury in the pump was brought about by alternately

exhausting and filling with air the reservoir C which held the mercury. This could be done by hand: the exhausting by connecting it with the water-pump through the tube β , the admitting air by opening the tap γ ; or, if preferred, by means of an automatic apparatus D through tubes $\delta\delta$. In this apparatus a three-way tap was turned through 90° by a lever, from one side of which was hung a cup fitted with a curved siphon and from the other a counterpoise, water being run into the cup through a flexible tube. The working of this apparatus was quite constant, and was accurately timed so that if it were left working for a known time the number of the strokes of the pump could easily be calculated. The mercury-reservoir C was placed at such a height that under atmospheric pressure the mercury would run over the top siphon α , care being taken that the distance from the siphon α to the T-piece c was considerably less than 30 inches. In the pump used it was 24 inches.

The mercury in the two McLeod gauges E and F was regulated for purposes of reading by coarse and fine adjustment-screws G; there was also a connexion with a movable mercury-reservoir H. The tube I contained pentoxide of phosphorus for drying purposes, and J was a vacuum-tube. This last was absolutely necessary, as it otherwise would have been utterly impossible to ascertain whether or not the apparatus was full of the gas under examination.

The gas to be examined was admitted through the tap K out of the chamber L. By means of the apparatus shown in the drawing any amount, large or small, of the gas could be admitted. The chamber L could be exhausted by the connexion through the tap M to the water-pump; a wash-bottle N containing mercury was interposed to prevent any diffusion backwards of air or water-vapour into the gas.

The amount of gas admitted was regulated by means of the siphon O which could be sealed by the mercury in the reservoir P. The mercury-level was adjusted by exhausting or filling with air the reservoir P in the same manner as with the reservoir C of the mercury-pump. The amount of gas admitted could, if desired, be measured in the gas volume-meter Q, which was designed on the model of the McLeod gauge. By means of this apparatus as small a

quantity of gas as $\frac{1}{50,000}$ of a cubic centimetre could be accurately measured and admitted.

The two gauges E and F were placed close together on the stand in order to bring them as much as possible under the same conditions of temperature and exhaustion, and were almost exactly of the same size. They consisted of a large volume-chamber (A) about 90 cub. centim. in capacity, with a pressure-tube (B) at the side and volume-tubes (C) and (D) at the top. The tube (B) was about $\frac{1}{4}$ inch internal diameter; (C) consisted of a somewhat large capillary tubing, and (D) of a tube of very small bore. (C) and (D) were each about 250 millim. long. The volume and pressure tubes were accurately graduated in millimetres, the divisions on each exactly corresponding. The zero-points of the scales were placed at the top of (D) and at the corresponding place on (B). (B) was graduated 500 millim. below and 250 millim. above the zero-point. The total length of the volume-tube was of course 500 millim. A trap (E) was sealed below the chamber (A) in order to more accurately determine the volume of the gauge.

The calibration of the gauge was a most important point and was most carefully done. Every centimetre division on the volume-tube was taken as a reading-point, making fifty possible. At each of these points the capillary depression of the mercury had to be determined, *i. e.*, the difference in reading between the mercury levels in the pressure and volume tubes when both levels were under the same pressure. In order to measure these differences the extreme top of (D) was drawn out before a blowpipe to a fine point and the tip cut off. The gauge was then placed in an exactly similar position to that which it would occupy when finally fixed on the stand. Mercury was run in from the bottom and readings taken in the pressure-tube, with the mercury standing at each of the 50 reading-points on the volume-tube. After this had been done both with rising and falling mercury, the actual volumes corresponding to each of the 50 reading-points on the volume-tube measured from its upper end were determined. The tip of (D) was sealed, and accurately weighed quantities of mercury were run in from a fine capillary tube which was pushed up (C) and (D). From the numbers thus

obtained the volumes represented by each reading-point could easily be calculated. Lastly, the total volume of the gauge from the top of (D) to the trap (E) was found by weighing the gauge empty and then filled with mercury. From the data thus obtained a table was constructed giving the capillary corrections and volumes in cubic centimetres for each of the fifty reading-points, due allowance being made for the meniscus. A column was also added of the values of R for each graduation, R being the ratio of the total volume of the gauge to the small volume at each point, or $\frac{V}{v}$. This ratio is used in calculating the vacuum in millimetres in the apparatus from a reading of the gauge. McLeod has shown that if a pressure p be read, and R be the ratio at a point on the gauge, then the vacuum will be found from the expression $\frac{p}{R}$, or, if a second approximation be required, from

$$p + \frac{p}{R}.$$

The method of calculating the numbers read on the gauges was to multiply each pressure by each volume.

The following table shows the accuracy to be expected :—

v' .	c .	v'' .	p' .	p in mm.	v in c.c.	pv .
120	7.2	127.2	-11.0	116.2	.129	14.99
100	7.1	107.1	+31.9	139.0	.107	14.93
80	7.1	87.1	+86.9	174.0	.085	14.91
70	7.1	77.1	+122.6	199.7	.074	14.94
60	7.1	67.1	+166.5	233.6	.064	14.93

In the first column v' are given the reading-points on the gauge volume-tube. In the second column c are given the capillary corrections ; under v'' the result of applying these corrections ($v''=v' \pm c$). Under p' the readings of pressure on the gauge, p the actual pressure exerted by the mercury

on the measured gas $p = v'' \pm p'$, plus or minus according to whether the reading of p' is above or below the zero-point on the pressure-tube (B). Then follow the volumes represented by the reading-points v' , and lastly the product of pressure and volume. In addition to this, if the original pressure in the apparatus before reading the gauge is over .1 millim. or thereabouts, this must be taken into account as the pressures found will be too small by this amount. The original pressure must therefore be found from the expression

$$\frac{p + \frac{p}{R}}{R}$$

as before shown and added to the values given in column headed p above.

When the calibration of the gauges was finished they were ready for use. In fitting up the apparatus it was absolutely necessary to seal all joints with a hand blowpipe so as to prevent any possibility of leakage. The tap K for the admission of the gas to be experimented on was an exceptionally good one of oblique bore. It was lubricated with gummy phosphoric acid, and though in constant use for over a year never once showed the faintest trace of any leak whatsoever.

During the experiments the mercury of the gas volume-metre Q was kept at a known point x , so that the volume of the apparatus to be exhausted was from the point x to the T-piece c of the mercury-pump, the tubes ee , together with the two gauges and the vacuum-tube J. The gauges when read had their volume-tubes jacketed with cold water; and fitted on gauge E on the diagram is shown the jacket-tube used in the experiments at high temperatures.

Whilst working with these gauges we noticed the following points amongst others. First, when the gauge is not in use, the mercury should be kept as close as practicable to the trap, for if it be kept some way below, the gas between the mercury and the trap will, on raising the mercury, inevitably be driven into the gauge and considerably disturb the accuracy of reading, even as much as seven per cent. error having occurred from this cause.

Secondly, the 'sticktion' of the mercury in the capillary

tubes of the gauges is very apt to introduce large errors into the results, especially at high vacua, when the pressures and volumes to be read are very small. To overcome this difficulty the tubes were continually tapped before reading, and many readings were taken both after ascent and descent of the mercury. That this was necessary may be shown by the fact that the before-mentioned capillary corrections when measured after ascent and descent of the mercury sometimes differed by as much as four millimetres.

It is also to be noted that the mercury must be raised very slowly, or gas will be trapped between the mercury and the glass. We also found it necessary to make the gauges of English lead-glass, as we found this to be the only glass that would stand the high temperature jackets without cracking.

EXPERIMENTS TO TEST THE ACCURACY OF THE MCLEOD GAUGE.

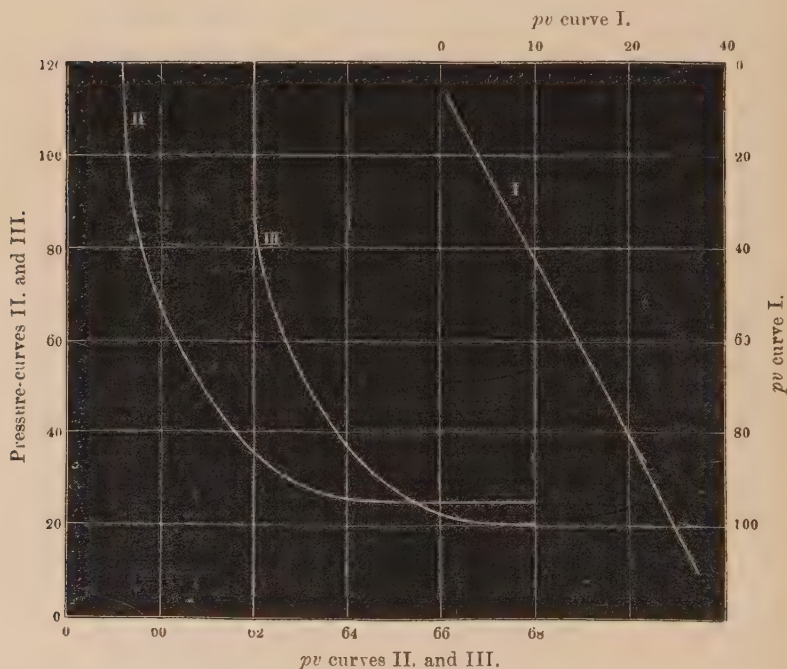
In order to determine once and for all the value of the McLeod gauge as a means of measuring vacua, some experiments were made with air. Many sets of readings were obtained, and they show the absolute failure of the gauge to measure vacua. It fails more and more as the vacuum improves. If the gauge had given trustworthy readings, the values of pv obtained at all reading-points should have been constant. We give here a set of values of pv measured at a moderate vacuum (p here refers to pressure in the gauge; not to the vacuum in the apparatus):—

p . millim.	pv .
4.1	100
4.1	81.83
4.1	69.921
4.3	67.25
4.6	59.57
4.6	41.78
4.9	33.47
5.0	23.09
6.3	15.09
8.0	9.427

The other sets of values of pv obtained during this exhaustion varied from 100-95, 100-74, 100-65, 100-38, 100-18, 100-14. In each of these sets the first and highest pv is raised to 100, and all other values in that set raised in proportion.

The set of values of pv given above, decreasing from 100 to 9 was plotted against pressures and the curve (No. I.) drawn which gives the value of pv constant for minimum pressure somewhere about 270. This gives a vacuum of 9 millionths of an atmosphere, instead of .3 millionth.

But the curve, as thus drawn, is not correct, for the decrease in the values of pv is due to two causes. First, to



the condensation of the gas on the glass as the pressure rises ; and secondly, to the fact that Boyle's law does not hold good for air at such low pressures. In addition to this, the surface of glass is uneven and not of uniform porosity. Two sets of

readings of the two gauges at the same vacuum were obtained with carbon dioxide. These two series were calculated for the same volume and were plotted against pressures. The two curves crossed at a point (Nos. II. & III.). Now this point, pressure and volume being the same, should be a point of equal surface, but it is very far from being so. We see, therefore, that equal pressures may condense quite different volumes of gas on two equal surfaces of glass; or, in other words, that two equal surfaces of glass may have quite different capabilities of absorbing a gas at a given pressure, owing apparently to want of uniform porosity. A curve drawn for a set of readings is, therefore, not to be depended upon. Indeed, with some gauges, the readings are so erratic that it is exceedingly difficult to draw a curve at all, and one of the gauges made for these experiments had actually to be discarded for this very reason. Such results as these put beyond a doubt the total worthlessness of the gauge as a means of measuring low pressures with air or with carbon dioxide.

With hydrogen, however, the case is different. After the apparatus was absolutely filled with hydrogen, the sets of values of pv read on the gauges were constant, at least within the limits of experimental error.

We give a type of the series of readings we obtained :—

p . millim.	pv .
24·5	1·00
29·5	1·00
37·3	1·01
49·3	1·01
75·2	1·02
100·3	1·01
152·3	1·00

Many series of values of pv were obtained, and they prove that hydrogen expands quite normally between the limits 650 and 2·5 millim. of mercury pressure. We found it impossible with any accuracy to make readings in the gauges with a

pressure smaller than 2.5 millim. These results also prove that hydrogen does not condense on a glass surface between these limits of pressure. By measuring the rate of exhaustion of an apparatus of known volume by a reservoir pump whose volume is also known, we found that hydrogen suffers no condensation on glass down to as low a pressure as .000076 millim.

Let the volume of the apparatus be called V and the volume of the pump V' , then the pressure after a stroke of the pump will be $\frac{V}{V+V'}$ times the pressure which existed before the stroke. This value may also be found experimentally by dividing the pressure after a stroke of the pump by the previously existing pressure. We have called this ratio the Factor of Exhaustion. It is evident that the constancy of this factor of exhaustion depends not on the expansion of the gas but on the possibility of condensed gas coming off the walls of the apparatus, in which case its value would increase. We made many series of measurements to obtain the factors of exhaustion, and found that they were quite constant and equal to theory down to the extreme limit of exhaustion.

We give here the results tabulated.

In the column headed ratio of gauge readings are given the ratios of the readings of the two gauges obtained at each measurement. As these, of course, ought to be constant, they may be looked upon as a measure of the experimental inaccuracies of the work, and may be used to correct the deviations observable in the values of the factors of exhaustion. In the last column are given the values of $\frac{V}{V+V'}$ calculated from the apparatus and pump volumes. Any change in these indicates a new apparatus.

The last series vary a great deal owing to difficulties of reading, and also to the fact of the extremely high vacuum, pumping is performed by diffusion. The presence of mercury-vapour makes no difference in these experiments at all. When the mercury is raised in the gauges and the pressure on the gas rises, the mercury-vapour becomes condensed, and readings are only made of the hydrogen in the apparatus. When the

No. of Stroke.	Vacuum.	Ratio of Gauge Readings $\frac{E}{F}$	Factor of Exhaustion from gauge E.	Factor of Exhaustion from gauge F.	Theory. $\frac{V}{V+V'}$
1st Series *.					
Preliminary.	4 millim.	1·0359			
I.	2·6 "	1·080	·5497	·5273	·550
II.		1·0555	·5431	·5512	"
III.		1·0663	·5436	·5345	"
IV.		1·0256	·5254	·5462	"
2nd Series.					
Preliminary.	4·9 millim.	1·015			
I.		1·049	·5396	·5374	·540
II.		1·055	·5363	·5366	"
III.		1·0476	·5376	·5414	"
IV.		1·0475	·5430	·5432	"
V.		1·0495	·5351	·5394	"
VI.	·11 millim.	1·0444	·5463	·5515	"
		Mean ...	·5395	·5416	
3rd Series.					
Preliminary.	·07 millim.	1·040			
I.	·0401 "	1·032	·5553	·5592	·557
4th Series.					
Preliminary.	Very high vacuum.	1·0397			
I.		1·051	·6429	·6362	·560
II.		1·053	·5547	·5543	"
III.		1·042	·6165	·6232	"
5th Series.					
Preliminary		1·0521			
I.		1·0494	·5374	·5388	·548
II.		1·054	·5413	·5386	"
III.	no connexion.	1·058			
IV.		1·0626	·5346	·5325	"
V.		1·060	·5389	·5401	"
VI.		1·0427	·5401	·5493	"
VII.		1·0368	·5395	·5426	"
VIII.		1·0366	·5412	·5412	"
IX.		1·0594	·5496	·5378	"
X.	·0068 millim.	1·083	·6289	·6462	"

* In this series it had not been noticed that it was necessary to keep the mercury as close below the trap as possible, so as to avoid impelling gas into the gauge on raising the level of the mercury, in order to close it.

Table (*continued*).

No. of Stroke.	Vacuum.	Ratio of Gauge Readings $\frac{E}{F}$	Factor of Exhaustion from gauge E.	Factor of Exhaustion from gauge F.	Theory. $\frac{V}{V+V'}$
6th Series.					
Preliminary.		1.0549			
I.		1.0741	.5639	.5486	.548
II.004	1.094	.5681	.5630	"
III.0024	1.101	.6530	.6494	"
7th Series.					
I.	Very high vacuum.5875	.5583	.590
II.7362	.7670	"
III.5857	.5912	"
IV.5634	.6012	"
V.6510	.5735	"

mercury is lowered again, mercury-vapour doubtless mixes with the hydrogen till a state of equilibrium is reached, the percentage of mercury-vapour depending on the pressure. In working the pump also the presence of mercury-vapour has no effect, for the pump-chamber when the mercury falls is empty of hydrogen, and if there is any hydrogen in the apparatus it will diffuse in through the mercury-vapour. This explains how it is possible to exhaust an apparatus filled with hydrogen so far that the pressure of the gas left is considerably below the pressure of mercury-vapour, though of course the actual pressure in the apparatus is not below that of mercury-vapour, for as fast as the hydrogen diffuses out of the apparatus into the pump, its place is taken by more mercury-vapour. Apparently, however, there is a limit to this, for we were not able to take out any more hydrogen than is represented by the last reading of the table above. The pressure of hydrogen in the apparatus was about .000076 millim., while the vapour-pressure of mercury is about .0002 millim.

An interesting calculation may be made with this value. If the gas under examination were air and not hydrogen, then a great quantity of air would have condensed on the

glass when the mercury was raised in the gauge to take the reading. If the curve (No. I.) were applied to this value, we should obtain the reading of the vacuum $\cdot 0000022$ millim. This curve, however, was obtained for air at greater pressure than the above, and the condensation would be still greater at $\cdot 000076$ millim., so that this is probably the highest vacuum that has yet been measured.

These results prove that hydrogen does not in any way condense on to a glass surface on rise of pressure, and that therefore in working a McLeod gauge with hydrogen all the gas in the gauge is measured and none lost by surface-condensation. The McLeod gauge is accordingly trustworthy to a certain extent when working with absolutely pure hydrogen.

With carbon dioxide, however, the case is different. Several series of factors of exhaustion were obtained with this gas, and it was found that they steadily increase in value as the exhaustion proceeds. This is owing to condensed carbon dioxide coming off the walls of the apparatus. It seems even possible to reach to a pressure which is equal to the "vapour-pressure" of the carbon dioxide which is condensed on the walls. For in a particular experiment the factors of exhaustion increased steadily till they reached $\cdot 997$, and 188 pumps more failed to make the slightest difference in the vacuum, as evidenced by the electric discharge in the vacuum-tube and by the gauge-readings. It would appear therefore that the pressure in the apparatus just equalled the pressure of the condensed carbon dioxide, and that as fast as the pressure was lowered by more pumping it was restored to its equilibrium by more carbon dioxide escaping from the pores of the containing walls. The vacuum was not very high, the *apparent* pressure being about one millionth of an atmosphere.

We found the converse of this when admitting measured volumes of carbon dioxide into a vacuum. In these experiments a gauge-reading was first taken and the pv calculated; then a known volume of carbon dioxide also calculated to pv was admitted. This last value multiplied by the ratio which the gauge volume bears to the rest of the apparatus will give the amount of carbon dioxide taken up by the gauge. This added to the previous value of pv read in the gauge ought to agree with the gauge-reading taken after the admission of

the carbon dioxide. But we found that the measured pv was always smaller than that calculated. This shows therefore that some of the carbon dioxide condenses.

We give one series of measurements together with the values calculated from the known volume admitted:—

Calculated.	Found.
4.4	4.2
7.9	6.8
9.4	9.1
9.1	7.4
11.9	11.5
16.7	15.9
21.2	19.6

These results are a further proof that the McLeod gauge is of no value in determining the amount of rarefaction of carbon dioxide.

We also found it very easy to exhaust all hydrogen out of the apparatus if there were any condensed carbon dioxide on the containing walls. When the pump was started at about 10 millim. pressure, the spectrum of the gas in the vacuum-tube was only that of hydrogen. As the exhaustion proceeded the factor of exhaustion steadily increased while hydrogen slowly disappeared from the vacuum-tube and carbon dioxide became in evidence, till in a short time all the hydrogen had been pumped out and only carbon dioxide remained.

These facts may give an idea of the great difficulties we met with in filling the apparatus absolutely with hydrogen. This was a most lengthy and tedious operation. In spite of the fact that the apparatus used for the hydrogen experiments never had carbon dioxide put into it, the glass and the phosphorus pentoxide nevertheless contained great quantities of this gas condensed on them, the removal of which took a very long time. First of all the apparatus was exhausted as highly as possible and then the glass, especially the phosphorus-pentoxide tube, was raised to a high temperature with a Bunsen-burner, the exhaustion being kept very high in the meantime. Hydrogen was then admitted, and the apparatus again exhausted, the heating being still continued. This was repeated until no further carbon dioxide could be brought off the walls by the heating in the vacuum and

until, after leaving it for a night, very highly exhausted, no spectrum of carbon dioxide was visible in the vacuum-tube when a current was passed. This process sometimes lasted a fortnight.

The foregoing results and the difficulties we met with in filling the apparatus with hydrogen emphasize our criticism on all previous work. For this fact of the condensation of carbon dioxide does not appear to have been noticed by previous experimenters. It would tend to make the read pressure too high, for carbon dioxide, being evolved from the glass with decrease of pressure, would mix with the gas under experiment and increase the apparent pressure. It is probably the reason why the product of pressure and volume has so often been found to increase with reduction of pressure.

To measure the expansion of hydrogen below the pressure of 2·5 millim. the thermal method was adopted. One of the two gauges was jacketed at a known temperature, and the expansion of the gas thus determined. Readings were taken on both the gauges, and the ratio of the two sets of values or pv obtained. When the mercury is lowered in the gauges the gas expands, and though its expansion below 2·5 millim. may be abnormal, this ratio of the values of pv remains the same. One of the gauges is then jacketed and the other read. This reading multiplied by the ratio before obtained gives the pv of the hot gas in the other gauge. The hot gauge is then shut off and allowed to cool, when it is read. The ratio of the readings of the gauge when hot and when cold is equal to the ratio of the absolute temperatures. To give an idea of the accuracy of the method we quote an example:—

Preliminary Readings to obtain the Gauge Ratio.

Gauge E.	Gauge F.
<i>pv.</i>	<i>pv.</i>
376·2	395·1
375·4	394·6
376·3	394·5
376·5	395·0
375·6	394·8
Mean = 376·0	Mean = 394·8

$$\text{Ratio } \frac{F}{E} = 1·05.$$

Gauge F was then jacketed with aniline vapour. Barometer 764·9 at 0° C.

Readings after jacket.

E.	F.
<i>pv.</i>	<i>pv.</i>
379·84	247·60
379·71	247·41
380·11	247·94
379·78	248·25
379·17	247·71
Mean = 379·71	Mean = 247·782
Temperature = 12°·5 C.	

When gauge F was hot the reading of gauge E was 379·71.

Therefore the reading of gauge F was
 $379·71 \times 1·05 = 396·80$.

Boiling-point of aniline at barometric pressure 764·9 millim.
 = 184°·66 C.

Therefore $396·80 : 247·782 :: x + 184·66 : x + 12·5$;
 $\therefore x = 273·741$.

\therefore Coefficient of expansion = $\frac{1}{273·741}$

Vacuum = 3·47 millim.

In making these experiments the readings were taken at the same reading-points throughout the whole operation so as to ensure accuracy. It will be evident that the volumes represented by the divisions on the gauge do not influence the result, and provided that the whole calculation is made from readings at the same points, the volumes at these points may be given any value whatever. The accuracy of the experiment therefore does not depend in any way on the accuracy of the volumes at the reading-points, but only of the pressures, which were very carefully read to within 0·1 millim.

The following coefficients of expansion of hydrogen were obtained :—

(T =temperature of jacket ; t =temperature of reading.)

Pressure.		T.	t.
4·7 millim.	$\frac{1}{273\cdot5}$	184 ⁰ ·66 C.	12 ⁰ ·5 C.
3·47 „	$\frac{1}{273\cdot74}$	184·33	13·8
·25 „	$\frac{1}{276}$	132·32	14·7
·096 „	$\frac{1}{297}$	132·27	17·3
·077 „	$\frac{1}{300\cdot5}$	132·33	16·3

The purity of the hydrogen in these experiments was satisfactorily proved by both the constancy of the gauge-readings in each experiment and by the factor of exhaustion being equal to theory.

If the above results be plotted on a curve it shows that hydrogen expands quite normally till a pressure of ·4 millim. is reached, when its elasticity increases with further decrease of pressure. Many other experiments were made, with similar results.

Having thus satisfactorily proved that this method of determining the thermal expansion of hydrogen is capable of giving accurate results, we proceeded to apply it to determining the expansions of oxygen and nitrogen at reduced pressures.

In the case of oxygen the gas was made by heating permanganate of potassium, it was washed in caustic potash and dried by means of sulphuric acid and phosphorus pentoxide. Oxygen proved to be an exceptionally difficult gas to deal with, as it was found impossible to determine its purity by the electric discharge in the vacuum-tube, as the presence of dust or other combustible material led to the formation of carbon dioxide. This method therefore was of no use, and the purity of the oxygen was determined by the result obtained, as will be seen further on.

The coefficient of expansion of oxygen was found to be, from very careful experiments :—

5·1 millim.	$\frac{1}{261}$,
5·3 „	$\frac{1}{260}$,
4 „	$\frac{1}{262}$.

These results are very fairly good, and being at such high pressures as 4 and 5 millim. may be said to demonstrate the absence of carbon dioxide, especially inasmuch as they give evidence of oxygen being too expansible, while carbon dioxide is the opposite. Each of these results, too, was obtained after a fresh filling of the apparatus, which in each case was most carefully done. Therefore the proof that they are measurements of the expansion of pure oxygen may be regarded as conclusive. As the results next obtained gave evidence that with decrease of pressure the coefficient of expansion still further increased, and as on the slightest sign of presence of carbon dioxide the apparatus was most carefully filled again with oxygen, there is no doubt that the expansion of pure oxygen was in each case measured. The presence of a small quantity of carbon dioxide would materially alter the results, as the value of the coefficient of expansion of this gas is so small at the pressures here dealt with.

The anomaly in the expansion of oxygen, first noticed by Bohr, was brought very strikingly under our notice in working with oxygen. The vacuum was at one time 1.4 millim., when, on a stroke of the pump being taken, the remaining gas, now at a pressure of about .75 millim., behaved in a most extraordinary fashion. For example, the two gauges E and F, which are of the same volume within .1 per cent., gave values of pv which, instead of being equal, had a ratio to one another of 1 to 8.8. We give the values :—

Gauge E.		Gauge F.	
<i>p.</i>	<i>pv.</i>	<i>p.</i>	<i>pv.</i>
12.3	= 6.00	100	= 53.3
17.9	= 6.04	106.1	= 53.1
25.6	= 6.09	113.3	= 53.0
37.5	= 6.03	125	= 53.2
<hr/> 6.04		<hr/> 53.15	

A large number of experiments were made, in which the gauges were continually opened and again closed and read, but the right ratio was not obtained until after 78 hours' rest. Then the readings in the gauge became normal, and an experiment was attempted to measure the coefficient of

expansion, but the equilibrium of the gas was instantly disturbed, and the result came out about $\frac{1}{1500}$. When the apparatus was exhausted beyond this particular point, the behaviour of the gas became quite regular again, and two measurements of expansion were made. This same anomaly was met with again in subsequent experiments.

The coefficients of expansion of oxygen we obtained were as follows :—

		T.	t.
5·1	millim. $\frac{1}{261}$.	132°·11	11
5·3	„ $\frac{1}{260}$.	132·0	11
4·0	„ $\frac{1}{262}$.	131·6	13
2·5	„ $\frac{1}{251}$.	132·1	9·4
	„ $\frac{1}{250}$.	131·8	11·5
1·4	„ $\frac{1}{233}$.	132·15	10·9
·083	„ $\frac{1}{244}$.	131·71	9·1
·07	„ $\frac{1}{240}$.	131·84	11

It will be seen, therefore, that the coefficient of expansion of oxygen decreases with decrease of pressure. Having a value of about $\frac{1}{261}$ at 5 millim., it increases steadily to where the change takes place. At a rarefaction greater than at this point, the value of the coefficient is again smaller, but it still appears to increase with further diminution of pressure.

It is difficult to account for the abnormal behaviour of oxygen as regards distribution in the gauges at a pressure of 0·75 millim. The only possible explanation appears to be that the temperatures of the two gauges must have differed to a small extent, and that the smallest difference in temperature produces quite an unusual disturbance in equilibrium.

Nitrogen was next experimented upon. The gas was prepared by absorbing the oxygen from air, first as far as possible by means of pyrogallate of potassium, and then by passing it over red-hot copper-gauze.

The experiments were carried out in the usual way, and there was no special difficulty connected with the filling of the apparatus with the gas.

The great difficulty in working with nitrogen was that

experienced in obtaining satisfactory and concordant results in measurement of the ratio between the gauge-readings preliminary to the jacketing. This difficulty increased as the vacuum improved, and it was found impossible to obtain results of any value whatever at a less pressure than .6 millim. The readings for the ratio were always taken with the utmost care, but in spite of this ratios sometimes differed amongst themselves as much as 2 per cent., which means a difference of 9 or more per cent. in the values of the coefficient of expansion.

The numbers obtained were as follows:—

Pressure.	T.	t.
5.3 $\frac{1}{304^{\circ}}$	132.55	8.8
4.97 $\frac{1}{303.8^{\circ}}$	132.16	9
3 $\frac{1}{301.6^{\circ}}$	132.42	8.5
1.1 $\frac{1}{304^{\circ}}$	131.7	14
.8 $\frac{1}{331^{\circ}}$	131.6	12.5
.6 $\left\{ \begin{array}{c} \frac{1}{355^{\circ}} \\ \frac{1}{343.5^{\circ}} \end{array} \right\}$	132.1	11.5
.6 $\left\{ \begin{array}{c} \frac{1}{377^{\circ}} \\ \frac{1}{323^{\circ}} \end{array} \right\}$	132.1	13
.6 $\left\{ \begin{array}{c} \frac{1}{301^{\circ}} \\ \frac{1}{327^{\circ}} \end{array} \right\}$	131.6	13
.6 $\left\{ \begin{array}{c} \frac{1}{371^{\circ}} \\ \frac{1}{343^{\circ}} \end{array} \right\}$	132.2	13

Mean of eight $\frac{1}{342.56}$ at .6 millim.

These last values of the coefficient of expansion are in four sets, each set being the result of an entire fresh filling of the apparatus with nitrogen. The two values in each set have been calculated with the two extreme values of the gauge ratio that have been obtained during the experiments at this pressure .6 millim. Though the results are not good, they nevertheless show that the coefficient of expansion of nitrogen for one degree Centigrade decreases with decrease of pressure.

To sum up the results:—(1) The coefficient of expansion

of hydrogen with temperature decreases as pressure is lowered. It is normal down to a pressure of 0.1 millim. (2) The coefficient of expansion of oxygen is greater than the normal one, being $1/262$ instead of $1/273$; it increases with decrease of pressure to $1/233$ at 1.4 millim. pressure; at 0.7 millim. pressure it is erratic; but at lower pressures it again becomes more constant, still showing, however, a tendency to increase as pressure is decreased. (3) With nitrogen the coefficient of expansion is lower than the normal ($1/304$) at pressures between 5 and 1 millim.; at lower pressures, like that of hydrogen, its coefficient of expansion decreases; that is the gas becomes more elastic. (4) So far as it was possible to experiment with carbon dioxide, its behaviour appears to resemble that of hydrogen and nitrogen; but owing to the tendency which it has to condense and cling to the gauge, trustworthy measurements were impossible to attain. These results corroborate those of Mendeléeff and Siljeström, although they are deduced from thermal expansion, while theirs were deduced from the compressibility of the gas. And Bohr's results as regards the abnormality of oxygen were also confirmed, although likewise by a different method.

If it may be taken for granted, then, that the rate of expansion of gases decreases with decrease of pressure, it is necessary to inquire why this is the case. From the point of view of the kinetic theory, pressure is caused by impacts on the walls of the containing vessel of the molecules which it contains, due to their translational motion. The internal motion does not give rise to pressure. If, on communicating to a gas energy, by raising its temperature, it does not respond by a sufficient rise of pressure, it appears to us that the conclusion is inevitable that its internal energy is increased to a greater than usual extent compared with its translational energy. It is perhaps idle to speculate on the extreme final state of rarefaction; but if this diminished rate of expansion were to continue to increase with tenuity, a point might conceivably be reached where all received energy would result in internal motion. Can this be the cause, or one cause, of phosphorescence in high vacua?

In his *Allgemeine Chemie*, second edition, vol. ii. p. 32, Ostwald treats of the limiting phenomena of volume-energy.

He suggests that if it be conceivable that the volume of a gas is increased indefinitely, the volume-energy obtainable from a gas would also increase infinitely, involving the consequence that from a finite quantity of gas an infinite amount of heat of constant temperature could be converted into kinetic energy. He therefore suggests that at some very great, yet finite volume, the pressure should become zero, and the gas should therefore refuse to increase its volume. Instead of the expression for Boyle's law, $p v = c$, $(p + k) v = c$, where $k = \frac{c}{v_{\max}}$, *i. e.* at a volume where $p = 0$. Such a supposition would place an upper limit to the atmosphere. Similar considerations are also applied by him to gravitational energy.

The abnormal behaviour of oxygen is, if not more, at least equally difficult to explain. Some profound change must take place suddenly at the pressure 0.7 millim. Whether this change is of the nature of dissociation or not, cannot readily be determined; but the spectra of oxygen appear to show that it is able to exist in several modifications at low pressures.

The work described appears to us very incomplete; yet it has not been for want of time and trouble spent on it. The experiments are of extreme difficulty, and it has taken close on two years to arrive at the results chronicled, imperfect as they are. We are, however, somewhat cheered to learn that the experience of Professor Mendeléeff has in this respect been like ours—that a short column of figures can express the results of the labour of years.

University College, London,
20th May, 1894.

DISCUSSION (June 8, 1894).

Prof. RAMSAY, in opening the discussion, recapitulated the chief points in the paper.

Siljeström in 1873 and Mendeléeff in 1875, he said, had both found that gases become less compressible than Boyle's law would give as rarefaction proceeds. Amagat in 1883 examined the subject, and concluded it was impossible to make measurements sufficiently accurate to decide the question one way or the other. In 1886 Bohr investigated

the compressibility of oxygen, and found its behaviour abnormal at about 0.7 millim. pressure. Van der Ven's experiments (1889) led him to conclusions opposite to those of Siljeström and Mendeléef, and those of Melander (1892) gave support to Van der Ven's results. To decide the question at issue the authors took up the subject, and their results confirm the conclusions of Siljeström and Mendeléef. They also prove that oxygen behaves abnormally at about 0.75 millim., as found by Bohr.

Prof. PERRY said some of the terms used in the paper required alteration. The word "elasticity" was employed in several senses, sometimes being used to denote " pv ," the product of pressure and volume, whilst at others its ordinary meaning was intended. He did not quite understand the connexion between pv and the thermal expansion to which the authors refer at the end of their paper. Taking Ostwald's equation for gases $(p+a)v=Rt$, he proceeded to show that the coefficient of expansion would be constant whether pv was constant or not.

Dr. BURTON said he had been accustomed to think that as pressure was reduced gases approached the simple or "perfect" state. It was very desirable that similar experiments be made on other gases to ascertain if any had constant coefficients of expansion. He failed to see why the internal energy should increase as the pressure decreases, unless under these conditions energy travels more by radiation than by conduction or convection.

The PRESIDENT, speaking of the adhesion of gases to the surface of glass, suggested experiments on the effects produced by varying the ratio of the surface to the volume of the gas. On the subject of distribution of energy he was inclined to agree with Dr. Burton's view rather than with the authors' suggestion. One would not be led by *a priori* reasoning to expect that the internal energy would increase with decrease of pressure.

Prof. RAMSAY, in reply, said that in the experiments on oxygen at about 0.75 millim. pressure the greater part of the gas was sometimes found in one McLeod gauge and sometimes in the other. Only after standing seventy-eight hours did the quantities trapped in the two gauges become equal.

The only explanation they could think of was that the temperatures of the gauges might not have been absolutely the same. Speaking of the suggested increase of internal energy with decrease of pressure, he said Prof. Dewar's experiments tend to show that there was little conduction through vacuous spaces.

The PRESIDENT thought Dr. Bottomley's researches had shown that radiation also falls off rapidly as the pressures become very small.

XX. *The Clark Cell when Producing a Current.* By S. SKINNER, M.A., Lecturer at Clare College, and Demonstrator at the Cavendish Laboratory, Cambridge*.

§ 1. *Introduction.*

THE electromotive force of the Clark cell when not producing any current has been frequently determined, and has been found to be of so constant a value that it is now used as a standard. These values of E.M.F. are for the cell when its poles are not united by a conductor. In the following an account is given of a series of experiments made on cells when producing currents, with the view of ascertaining, (1) how far the total electromotive force round the circuit differs from that of the open cell, and (2) how this new value for the E.M.F. changes when the current is maintained. If these quantities can be accurately measured, it follows that a cell might be used for producing currents of known value. Some experiments have been made on subject (2) by Threlfall and Pollock (Phil. Mag. November 1889), and their results are compared with mine in Sect. 8.

§ 2. *The Cells.*

The experiments were made on three cells, all much larger than the ordinary Board-of-Trade pattern of Clark cell.

Cell B, made July 1891, is the cell no. 90 described on p. 558 of the paper by Mr. Glazebrook and the author, Phil. Trans. 1892, A. The area of its exposed zinc surface is, approximately 14·4 square centimetres.

* Read June 22, 1894.

Cell L, made November 1892, is a much larger cell fitted up in a cylindrical jar 22 centim. high and 13 centim. in diameter. The zinc plate exposes an area of about 95 square centimetres.

Cell N, made July 1893, is intermediate in size and exposes about 29 square centimetres of zinc surface.

In all three cells the zinc plate, a piece of common zinc sheet, is placed horizontally, and they have the same E.M.F. within 2 parts in 5000.

§ 3. *The Effect of Uniting the Poles of a Cell.*

Let a cell of electromotive force E and internal resistance R have its poles joined by a wire of resistance r ; then, providing R and r are constant, and there is no polarization, the potential-difference between the poles will be $\frac{rE}{R+r}$. If, however, there is polarization, then this potential-difference will be $\frac{re}{R+r}$, where e is the value of the electromotive force required to produce the observed current.

The value of $-(E-e)$ is the electromotive force of polarization.

In the large Clark cells described above E and e are nearly equal when the current is not larger than .01 ampere; this small difference is the subject of the following measurements. To obtain it, it is clearly necessary to find the value of the potential-difference $\frac{re}{R+r}$, and of the resistances R and r . The measurements for R are contained in Sect. 4; r consisted of thick wire coils or of a special wire resistance immersed in a large tank of paraffin oil; and the measurements of the potential-differences are contained in Sect. 6.

We shall now give an illustration, taken from an actual experiment, of what happens when the poles of a cell are united. On July 25th the cell L had an electromotive force, with its poles open, represented by 5009 on the compensator. The poles were then joined by a resistance of 1000 legal ohms, and their potential-difference, taken as quickly as possible, was then rather more than 4983 and rather less than 4984. Then a resistance of 500 legal ohms was substituted for the

1000 ; the potential-difference fell to 4959. Next, with 200 legal ohms the potential-difference was 4885. Lastly, the poles were opened, and the electromotive force of the cell was found to be 5009.

It is seen from these numbers that the cell recovered its electromotive force entirely after the various operations, and this is a typical instance of the behaviour of the cells. It should be mentioned here that these tests, as well as tests on two other cells, were made in the interval between the two sets of resistance observations recorded in the column of the table § 4, headed " July 25th, Before—After."

§ 4. *Measurement of the Internal Resistance of the Cells.*

The important determination of the resistance of the cells was made by the method of Opposition, and by the use of an Alternating Current. By opposing any two of the cells, the resulting electromotive force was so small that, making them an arm in a Wheatstone's arrangement, there was no deflexion in the bridge-galvanometer. The bridge was fed with an alternating intermittent current by means of the commutator used by Mr. T. C. Fitzpatrick in his electrolytic measurements, B. A. Report, 1886, p. 328.

In this method the commutator is arranged to supply the currents in the galvanometer-circuit always in the same direction, so that an ordinary sensitive mirror-galvanometer can be used. The drum of the commutator has on each circular face eight insulated sectors of brass, those on one side being larger than those on the other. The larger sectors are connected by brushes to the battery-circuit, and the smaller to the galvanometer-circuit. They are arranged so that the battery connexion is always closed before that of the galvanometer, and is always broken after that of the galvanometer. A more complete description of the commutator, which works excellently, will be found in the paper already mentioned. Two or three Leclanché cells were used as the battery.

The method of connecting two cells together so as to have small resulting electromotive force is particularly applicable in the case of Clark cells, for they may be obtained of nearly equal electromotive force. In the case of the cells we are

discussing, as mentioned in § 2, the greatest difference was never more than 2 in 5000.

The errors to which this method of measuring battery-resistance is liable are two : first, from self-induction, and second, from polarization at the electrodes. The only conductor containing self-induction of any magnitude is the galvanometer-coil, and as the method is a zero method this does not matter. The second error is eliminated by using an alternating current. However, following Fitzpatrick's method, tests were specially made for polarization by varying the ratio of the arms and by varying the speed of the commutator. For instance, on one occasion the resistance was between 11·0 and 11·1 with the usual speed for working; when the speed was more than doubled, the resistance retained the same value.

The three cells were measured in pairs, and the results in legal ohms are given in the following table, where C is the resistance of the connecting wires.

The words "Before," "After," refer to the relation of these measurements to those recorded in § 6.

Cells.	July 20th. 16°·8.	July 23rd. 18°.	July 24th. 17°·8.	July 25th. 17°·8.	
	<i>After.</i>	<i>Before.</i>		<i>Before.</i>	<i>After.</i>
N+B+C	13·20	12·8	13·1	13·25	13·11
L+B+C	11·69	10·8	11·05	11·15	11·10
N+L+C	11·04	10·7	10·9	10·98	10·90
C	0·93	0·93			
From which are calculated the following values of resistance :—					
L	4·30	3·88	3·96	3·97	3·98
N	5·81	5·88	6·01	6·07	5·99
B	6·46	5·99	6·16	6·25	6·19

The temperatures are those of the water-bath in which the cells stood ; the cells were not moved during the whole of the measurements. It will be noticed that the resistance of the cells is lower at high than at low temperature. This agrees with the fact that electrolytes decrease in resistance with increase of temperature.

§ 5. *The Resistances, and Apparatus for Comparison of Electromotive Forces.*

The compensating apparatus was the same as that described in § 8 of the paper by Mr. Glazebrook and the author already quoted. However, in the place of the Leclanché cells there described to produce the main current, I used one or two large Clark cells. The reason for this change arose from the irregular behaviour of the Leclanché cells when changes were made in the amount of current taken from them. The results of eleven series of observations were rendered useless on this account. When only one Clark was used in the main circuit, the standard cell for reference was a Helmholtz mercurous-chloride cell, § 7. When two Clark cells were used, the standard was some other Clark cell which was kept at rest.

The circuits, through which the currents from the cells under test were taken, consisted of thick wire coils from a legal ohm resistance-box for the values 1000, 500, 200 legal ohms, and of a german-silver wire of 147 legal ohms wound on an ebonite frame, which was placed in a tank of paraffin oil. This german-silver wire was always used when the current was maintained for any length of time, as from its construction its temperature could be very accurately observed.

§ 6. *Determination of the Electromotive Force of Polarization.*

By means of the method described in § 5 the results in the following table were obtained. The units of electromotive force are approximately $\frac{1.4}{5000}$ volts.

Cell and Date.	E.M.F. of cell open = E.	Potential-difference for the cell producing approximately :—			
		·0014 ampere $r=1000$ legal ohms.	·0028 ampere $r=500$ legal ohms.	·007 ampere $r=200$ legal ohms.	·01 ampere $r=147$ legal ohms.
L. July 20...	5010	4837
L. „ 23...	5009	4985	4961.5	4890.5	
L. „ 25...	5009	4983.5	4959	4885	
N. „ 25...	5007.5	4959.5	4912		
B. „ 25...	5007	4971.5	4938.5	4841	

The simplest way to examine these results will be to calculate the electromotive force required to produce the observed current, when the cells are producing currents of different values. Using, then, the equation

$$e = \frac{R+r}{r} \times \text{potential-difference,}$$

with values of R from § 4 and of r from § 5, we have the following values of e :—

	E.	e for '0014 ampere.	e for '0028 ampere.	e for '007 ampere.	e for '01 ampere.
L	5010	4981
L	5009	5005	5001	4988	
L	5009	5005	4999	4983	
N	5007·5	4989	4971		
B	5007	5003	5000	4990	

From which we obtain the values for $E-e$, the electromotive force of polarization being $-(E-e)$.

	$E-e$ for '0014 ampere.	$E-e$ for '0028 ampere.	$E-e$ for '007 ampere.	$E-e$ for '01 ampere.
L	29
L	4	8	21	
L	4	10	26	
N	18·5	36·5		
B	4	7	17	

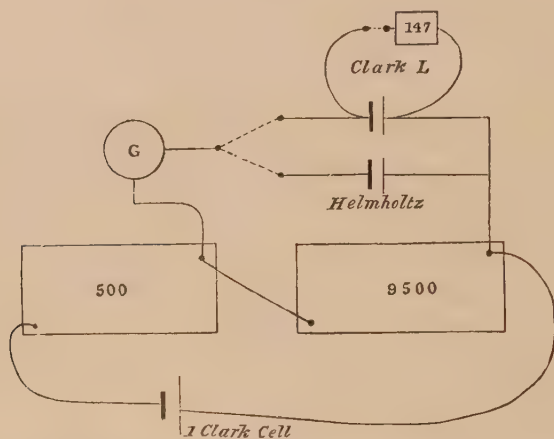
It will be observed that for a given cell the electromotive force of polarization is directly proportional to the current-density.

§ 7. *Effect with Time, the Current being maintained.*

The experiments to be described in this section show how the potential-difference varies when the cell is allowed to produce a current for some time. For these experiments the standard of reference was a set of Helmholtz cells described

in the paper quoted above, p. 618 ; they were immersed in a tank of paraffin oil. On January 17th they were submitted to a very rigorous test for constancy, extending over four hours, a Clark cell being the standard. It is not necessary to say anything further about them.

Fig. 1.



The arrangement used in the experiments is illustrated in the accompanying diagram (fig. 1), which clearly explains itself.

A single Clark cell was used in the main circuit for the reason that it is so much more steady than the usual two

Time.		E.M.F.	Temperature. Oil.	Temperature. Water.
h	m			
11	14	Helmholtz 6890+	13°	12°
12	15	" 6891-	13	12.1
2	27	" 6891+	13.2	12.3
2	33	Clark L through 147 l. ohms.		
2	36	Clark L 9447+		
2	37	" 9447+		
2	38.5	" 9447+		
2	49	" 9447		
2	59	" 9446+		
3	5.5	" 9446		
3	13	" 9446-		
3	20	" 9445+		
3	29	" 9445-		12.4
3	33	Clark off		
3	35	Helmholtz 6891+	13.3	
4	4	" 6891+	13.4	12.5

$$\text{Unit E.M.F.} = \frac{\text{E.M.F. Clark}}{10,000}$$

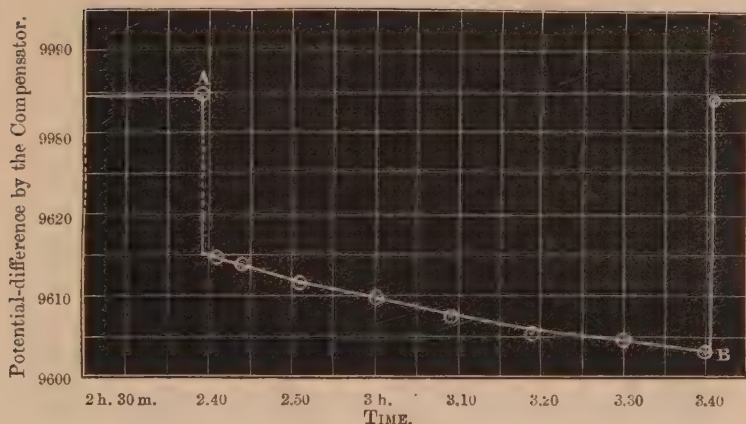
Leclanché cells, *vide* § 8. The complete results of a single experiment are given in the foregoing table.

Another set of observations is given in the accompanying diagram (fig. 2).

Fig. 2.

Jan. 16th, 1893. Temperature 12° .—At A, the Clark cell L was short-circuited by 147 ohms. At B, the circuit was broken.

$$\text{Unit of E.M.F.} = \frac{\text{Clark}}{10,000}$$



The four experiments made by this method gave an average fall of 7 units in the hour, and from the table § 6 we have the polarization on immediately making contact equal to 29 units $\left(\frac{\text{Clark}}{5000}\right)$, or 58 of our present units.

The polarization, or $-(E-e)$, for a current-density of $\frac{.01 \text{ ampere}}{100 \text{ centim.}^2}$ for cell L may at any time be expressed approximately by

$$-(58 + 7t),$$

where t is the time in hours, and the unit of E.M.F. is $\frac{\text{Clark}}{10,000}$. Expressed in volts this is

$$-(.00834 + .001 t).$$

It is deduced from experiments on cell L, and only indicates the general order of magnitude of the effect with the other cells.

§ 8. *Conclusion.*

Throughout the calculations it has been assumed that the total electromotive force round the circuit is equal to that of the cell at rest; and therefore that the electromotive force overcoming polarization can be obtained by subtracting from the electromotive force of the cells at rest the observed current. With the exception of small Peltier effects, I know of nothing against this assumption.

The results of the experiments are :—

- (a) The electromotive force of polarization varies directly with the current-density in a particular cell.
- (b) The electromotive force of polarization slowly increases when the current is maintained.

From the magnitudes of the quantities found in these experiments, it follows that small currents of approximately known value can be obtained by the use of large Clark cells of small internal resistance, which may be neglected in comparison with the large external resistance. The experiments show that the large cell L when producing .01 ampere was not at all disturbed. This corresponds to a current-density .01 ampere / 95 (centim.)². Now in a Board-of-Trade pattern Clark cell there is generally an exposed area of zinc equal to 2 (centim.)², and as the current taken is never greater than $\frac{1.43}{10,000}$, a 10,000 ohm coil being used in series with it, it follows that the current-density with this value of current is very much below that which has been found to be safe in these experiments.

In the experiments of Threlfall the sign of the term depending on time was found to be negative. In some of my earlier experiments it appeared to be negative, but this was traced to irregularity in the working of the compensator; and the effect has always been positive since the Clark cells have been used in the place of Leclanché, *vide* § 5.

XXI. *A New Integrating Apparatus.* By A. SHARP, B.Sc.*

(Abstract.)

THE paper describes an improved form of harmonic analyser, giving the amplitude and epoch of each constituent term, the mechanism of which is an inversion of that described in a communication made to the Society on April 13, 1894 (*ante*, p. 89). Numerous drawings accompany the paper, showing the various parts in detail. The mechanism is also shown to be applicable for integragraphs, and by suitable modification may be employed for mechanically integrating differential equations of various forms.

XXII. *Magnetic Shielding by a Hollow Iron Cylinder. Simplest Case.* By JOHN PERRY, F.R.S.*

I CONSIDER going and return electric conductors each at a distance a from the axis in a diametral plane of the hollow cylinder, the current in each being C .

As to the inducing magnetic potential, all over one half of the cylindric surface of radius a the potential is constant, πC , and all over the other half it is constant, being $-\pi C$. At a point P whose distance from the axis is r , the angle made by the axial plane through P and the plane through the conductors being θ , it is evident that V , the inducing potential, is

$$V = 4C \left(\frac{a}{r} \sin \theta + \frac{1}{3} \frac{a^3}{r^3} \sin 3\theta + \frac{1}{5} \frac{a^5}{r^5} \sin 5\theta + \&c. \right),$$

as this becomes $+\pi C$ or $-\pi C$ where $r=a$, and also satisfies $\nabla^2 V = 0$.

Let the coefficient of $\sin n\theta$ in V be denoted by $A r^{-n}$; let the corresponding coefficients be $A_1 r^n + A r^{-n}$ for the total (induced plus inducing) potential inside the tube; $A_2 r^n + B_2 r^{-n}$ total in the iron and $B_3 r^{-n}$ in outside space. Let the inside

* Read June 22, 1894.

and outside radii of the iron cylinder be a_1 and a_2 . Then, on stating the equality of the potentials just inside and just outside the two surfaces, and also that the normal induction is the same on both sides, we have four equations, which enable the coefficients A_1 , A_2 , B_2 , and B_3 to be calculated. The two important ones are

$$B_3 = 4\mu A / \{(\mu + 1)^2 - e(\mu - 1)^2\},$$

where e stands for a_1^{2n}/a_2^{2n} ,

and $A_1 = -A\rho(1-e)/a_1^{2n}(\rho^2 - e)$,

where $\rho = (\mu + 1)(\mu - 1)$.

If we take $a_2 = a_1 + t$, and t is small, since μ is large in iron, we have approximately

$$B_3 = A / \left(1 + \frac{1}{2}\mu n \frac{t}{a_1}\right).$$

The higher terms are unimportant. Taking the first: the unshielded potential was $4Ca r^{-1} \sin \theta$, and it is converted by shielding into $4Ca \sin \theta / r \{1 + \frac{1}{2}\mu t / a_1\}$.

Thus, taking $\mu = 1200$, $a_1 = 150$ cm., $t = 5$ cm., the first and most important term is reduced to the 1/21st part of its unshielded value. The other terms are reduced to 1/61st, 1/101st, 1/141st, &c., parts of their unshielded values.

In this case the potential inside is very little less than when there was no iron, A_1 being $-A/a_1^{2n}$ for all values of t until t is small; of course A_1 is 0 when t is 0.

It is easy to extend the reasoning to several enveloping cylinders of iron, or to the case of any distribution of inducing potential which does not vary in a direction parallel to the axis.

PHYSICAL SOCIETY OF LONDON.

ABSTRACTS OF PHYSICAL PAPERS FROM FOREIGN SOURCES.

FEBRUARY 1895.

GENERAL PHYSICS.

115. *Interruptor for Large Induction-Coils.* **F. L. O. Wadsworth.** (Am. J. Sc. pp. 496-501, December 1894.)—This consists of a brass wheel about 6 in. in diameter, with two insulating and two contact segments symmetrically placed in its circumference, and mounted directly on the shaft of a small electric motor making about 1200 revolutions per minute. Two copper brushes are arranged to bear, one on the hub of the wheel, the other on its circumference. The hub, web, and flanged felloe of the brass wheel are cast in one piece and turned up true all over, so as to be perfectly balanced, even at high speeds. The insulating segments are made of cut slate. Each takes up 50°, and is cut so as to fit the curve of the outer face. They are bevelled off to the outside, and are held in place by two brass or copper segments 130°. A piece of sheet platinum is inserted between the slate and the brass at the two places where the heavy spark of the break occurs. This interruptor was constructed for Prof. Michelson's Geissler-tube experiments, and has worked very satisfactorily. E. E. F.

116. *The Galilean Falling-Groove for Physical Demonstrations.* **P. Volkmann.** (Zschr. phys. chem. Unterr. 7. pp. 161-166, 1894.)—The groove used consists of a slightly grooved iron rail mounted on the edge of a plank 3 m. long. The face of the plank turned towards the audience is divided into decimetres, and supplied with movable tin pointers for indicating the position reached by the rolling sphere at each beat of the metronome.

The zero end can be clamped in any position above or below the horizontal, or can be raised by a lever. For determining the velocity acquired after any given time the lever is quickly and gently lowered until the groove is horizontal, this position being fixed by a stop. The equal velocities of different masses may be demonstrated by letting equal spheres of different materials roll down together, placing one of them first behind and then in front of the other. The different modes of transformation of energy may be exhibited by equal spheres, solid and hollow respectively, which have different velocities according to their moments of inertia, and hence also according to the different amounts of rotational energy acquired. E. E. F.

117. *Mixing of Liquids.* **J. de Kowalski.** (C. R. 119. pp. 512-513, 1894.)—Experiments to test van der Waals' theory that two liquids which do not ordinarily mix at a given temperature will mix under sufficient pressure, give negative results though 1000 atmospheres were reached. But *three* liquids—ethyl alcohol, isobutyl alcohol, and water, which completely mix above $22^{\circ}4$ but below $22^{\circ}4$ form two distinct liquids under ordinary pressure—completely mix at $19^{\circ}5$ under 900 atmospheres, separating however on fall to 19° (with momentary formation of a small cloud before the appearance of the meniscus), and not mixing again even under 1500 atmospheres. R. E. B.

118. *Relation between the Vapour-Pressures of Water, Ice, and a Freezing Saline Solution.* **A. Ponsot.** (C. R. 119. pp. 731-733, 1894.)—The vapour-pressure of a saline solution freezing at T is that of ice at T . By consideration of two reversible cycles, one of which is incompletely described, the following relation is deduced:—

$$RT \log (F/f) = J[l_0(1 - T/T_0) - (C - c)\{T_0 - T - T \log (T_0/T)\}],$$

where l_0 is the latent heat of fusion at the triple point T_0 , C and c the specific heats of water and ice, J the mechanical equivalent of heat, and R the constant for steam regarded as a perfect gas. Tested by comparison with Jühlin's and Fischer's observations, this relation gives very satisfactory results. For very dilute solutions it is equivalent to Guldberg's law,

$$1 - f/F = (T_0 - T) \times J l_0 / RT_0^2. \quad R. E. B.$$

119. *Simple Chronograph Pendulum.* **C. Barus.** (Am. J. Sc. pp. 396-397, Nov. 1894.)—The apparatus consists of a seconds pendulum which at the end of each swing in one direction comes into contact with a light pendulum of longer period. During contact a current passes from one bob to the other, through the chronographs, and through a small electromagnet which exerts a

pull upon an armature attached to the seconds pendulum above the knife-edge. The contact is reduced to 0.1 sec. by a platinum spring attached to the smaller bob, and the latter is prevented from following the larger bob by a stop.

E. E. F.

120. *Hardness and Elasticity of Glass.* **F. Auerbach.** (Wied. Ann. 53. pp. 1000-1038, 1894.)—Fourteen different kinds of glass, manufactured by Schott of Jena, were tested for hardness and elasticity with reference to their chemical composition. It was found that the "absolute hardness" of the glasses investigated differed very widely, varying from 173 to 316, or between 5 and 7 of Mohs' scale. The hardness as determined by scratching corresponded to the absolute hardness in most, but not in all cases. But the scratching method is too complicated and untrustworthy for scientific purposes. For almost all the glasses the hardness could be represented as a linear function of the "hardness coefficients" of the various constituents. Alumina had the highest of these, whereas lime and soda had negative coefficients. Hardness is not proportional to modulus of elasticity, the ratio varying between 0.029 and 0.046.

E. E. F.

121. *Aggregation of Crystals near the Surface of lighter Liquids than they.* **Lecoq de Boisbaudran.** (C. R. 119. pp. 392-393, 1894.)—If fragments of crystals, of greater density than their solutions, are placed in these solutions, some near the surface, some on the bottom, the crystals on the bottom will as a rule grow, and the others not disappear. If, however, a saturated solution of carbonate and hyposulphite of soda, dissolved simultaneously, is further saturated with ($\text{Na}_2\text{S} + 9\text{H}_2\text{O}$), of which considerable quantities will pass into solution, and fragments are similarly distributed, the whole of the sulphide will, after days or weeks, be found on the little support near the surface, although the crystallised Na_2S is heavier than the complex solution. It would appear, therefore, that the solution of the three salts is less dense than that of the carbonate and hyposulphite, and that the addition of the third salt produces dilatation. The motions of dust particles and gravity determinations prove this to be correct; the densities were 1.4386 before and 1.4179 after the addition of the sulphide at $25^\circ.5$. The experiments can also be made with a solution of ($\text{Na}_2\text{S} + 9\text{H}_2\text{O}$) only.

H. B.

122. *Crystallisation at Low Temperatures.* **Raoul Pictet.** (C. R. 119. pp. 554-557, 1894.)—As a rule, crystallising liquids have a constant temperature. Certain substances, however, which crystallise at low temperatures, behave anomalously: among these are pure chloroform, and more or less diluted alcohol, sulphuric acid, hydrochloric acid, &c. When a glass tube filled with one of these substances is brought into a bath whose temperature is

below that of its freezing-point, there takes place, between the liquid molecules in motion, the already solidified molecules, and the walls of the glass, an exchange of heat both by conduction and by radiation, a heat-wave being produced by the molecular shocks while the substance passes from the liquid into the solid state. By integrating between the moments when the shock commences and when the crystal has been formed, we can determine the latent heat of crystallisation. But we have to distinguish between athermanous and diathermanous bodies. In a substance of the first class, as water, all internal heat escapes through the already solidified particles to the wall and the surrounding medium, the quicker the colder this medium is. Radiant heat is changed into actual heat, and also removed by way of conduction. The temperature therefore remains constant although the liquid tends to maintain the highest temperature compatible with crystallisation. In a diathermanous liquid the radiant heat finds no obstacle in the crystals, but escapes at once; and any heat from outside heats the whole mass, not merely that in immediate contact with the crystals. The liquid directly in contact is alone at the true temperature of crystallisation; within the crystals the temperature is higher, in the liquid lower. This difference increases with the difference between the temperatures of the liquid and the medium. As below -70° C. all bodies become more and more diathermanous, it is not astonishing that liquid chloroform, which deposits crystals at -83° , should indicate a temperature of $-68^{\circ}5$, while the thermometer outside marks -120° or -130° C. In order to observe the true temperature of crystallisation for freezing-points below -50° , the medium outside should therefore be as warm as practicable, and the crystallisation should proceed very slowly. As soon as the temperature sinks outside, it will rise within the liquid. H. B.

123. *Mercurial Telethermometer.* **M. Eschenhagen.** (Zschr. Instrumk. pp. 398-404, 1894.)—A fine platinum wire is threaded through the bore of a mercurial thermometer, and is sealed where it enters and leaves the tube. As the meniscus rises and falls it encroaches or recedes along the wire, exposing it more or less, and thus varying its resistance. These resistance-changes are measured at the distant station, and the temperature is deduced from the results. Some attempt is made to compensate for the many error-sources to which such a system is open; and an accuracy to $0^{\circ}1$ C. is claimed. R. A.

124. *Surface-Tensions of Solutions.* **V. Monti.** (N. Cim. 36. pp. 259-263, 1894.)—The author measures the S.T. of aqueous solutions of salicin, phenol, and alcohol, and finds that in each case the S.T. of the solution is less than that of water, the solution of phenol in particular having a much lower S.T. than water. The measurements are made by the capillary-tube method and by counting the drops from a pipette. The author concludes from

his experiments that the statement of Jaeger, that for dilute solutions the increase in the capillary constant is proportional to the osmotic pressure, does not hold for solutions of indifferent substances.

J. W. C.

125. *Function a in Van der Waals' Equation.* **G. Bakker.** (Zschr. phys. Chem. 14. pp. 664-671.)—Van der Waals' equation,

$$p = \frac{RT}{v-b} - \frac{a}{v^2},$$

is treated from the thermodynamical standpoint, and the author concludes that the function a decreases as the temperature rises. At high temperatures the curve showing a as a function of the temperature is convex to the temperature-axis.

W. C. D. W.

126. *Theory of Stefan's Calorimeter.* **W. Kutta.** (Wied. Ann. 54. pp. 104-129, 1895.)—This calorimeter, made of two concentric and coaxial right circular cylinders which are closed by ends perpendicular to the axis, has been used to determine the conductivity of both gases and liquids. The heights of the cylinders being H, h , and radii R, r , and the conductivity of the enclosed fluid being k , the stationary flow of heat per second per degree of temperature-difference has been taken as approximately

$$k\{\pi(H+h)\log_e(R/r) + \pi(R+r)^2/2(R-r)\} :$$

by the use of conjugate functions after Kirchhoff's method it is shown that the coefficient of k should be diminished by $\kappa(R+r)\log_e 2$, where κ lies between 3 and 4 and may be taken as $3\frac{1}{2}$. This correction raises Winkelmann's value of k for air at 0° by 3 per cent. to 5.715×10^{-5} .

R. E. B.

127. *Thermal Expansions and the Compressibility of Solutions.* **G. Tammann.** (Zschr. phys. Chem. 13. pp. 174-186, 1894.)

—The thermodynamic surface for a solution nearly coincides with that for its solvent if it be subjected to a pressure Δk instead of one atmosphere. Thus, if $\phi(p, v, t) = 0$ represent the surface for the solvent, $\phi(p + \Delta k, v, t) = 0$ will give that for the solution. This is confirmed by the consideration of the work of Marignac, Amagat, Despretz, and Rosetti on the isobars for water and aqueous solutions, and of Tait and Amagat on the compressibility of water and its solutions for the isothermals.

W. C. D. W.

128. *Coloured Waters of the Grottoes of Capri, of Ice-hollows in Switzerland, and of Yellowstone Park.* **H. W. Vogel.** (Wied. Ann. 54. pp. 175-177, 1895.)—Twenty years ago Vogel noticed in the spectrum of the water of the Blue Grotto a peculiar absorption-band between b and E and the absence of the red and yellow up to D . The "Grotto Verte" is rather a tunnel with

many clefts, with a yellowish rock and blue-green water; this has no red in the spectrum, but there is no trace of the absorption-band between *b* and E. Near the entrance of this grotto and, as can be seen from an elevated spot, all round the island of Capri, little patches of azure-blue water can be noticed, which are stationary in still water; all these blue waters have the same spectrum as the water of the Blue Grotto. The water of the "Grotto Rosso" is not red at all. Not only the glaciers, but also holes made with an alpenstock in the freshly fallen "firn" snow, show a bluish tint, with extinction of the red in the spectrum. The green water of certain geyser-basins in the Yellowstone Park show Schönn's water-bands in the red and orange. Moran, the artist of Heyden's geological expedition, has painted this green water a brilliant ultramarine, which Vogel never perceived. In his opinion Moran's tints are far too brilliant. H. B.

129. *Resistance of the Air*. **E. Vallier**. (C.R. 119. pp. 885-888, 1894.)—The resistance which a gas opposes to the motion of a plane varies as the surface, the density of the gas, its pressure, and a certain function $\frac{1}{g}f(v)$ of the velocity of the plane. Newton supposed the square of the velocity to enter; then other powers were suggested; for velocities above 400 m. the function was supposed to be $v^2Kf(v)$. According to Vallier, however, the term $K(v)$ is very complex. Fairly constant for smaller velocities, it increases after $v=140$ m., specially near 340 (velocity of sound), and does not become constant even at the maximum speeds experimented with, 1200 m. The curves published by Krupp in 1890, referring to velocities of 1000 m. of oblong projectiles, and by Gibert on trials made at Gâvre, show that the shape of the head of the projectile, ogive, is of importance. The practical rule is:—for velocities above 330 the resistance can be represented by a straight line; for velocities between 330 and 100 by a curve of degree $\frac{5}{2}$; below 100 by one of the second degree. More accurately:—

$$\rho = \frac{1}{g} H(v-a) \quad \text{for } v > 330;$$

$$\rho = \frac{1}{g} H'v^{\frac{5}{2}} \quad \text{for } 330 > v > 100;$$

$$\rho = \frac{1}{g} H''v^2 \quad \text{for } v < 100.$$

The constants H, a depend upon the angle γ of the ogive. For $\gamma=41^\circ.5$,

$$H \text{ is } = 0.125, a=263; 330^{\frac{5}{2}} H' = H(330-a); H''=10 H'.$$

To pass over to other angles, we have to multiply H by a factor $i(v)$, which gives the following values:—

γ	=	31°	33°·6	36°·9	41°·5	48°·2
$i(v)$	=	0·67	0·72	0·78	1·00	1·10

These figures represent the differences between the pressure in front of the projectile and the counter pressure exercised by the eddies behind it.

H. B.

130. *The Resistance of the Air.* **C. Chapel.** (C. R. 119. p. 997, 1894.)—Chapel remarks that he deduced Vallier's law that for pressures above 330 m. the resistance of the air can be represented by a straight line long ago from experiments made in Russia and in Germany, and that Sarrau came to the same conclusion from his researches at Gâvre. From recent trials conducted in Germany, Chapel concludes that this law is correct for velocities up to 1000 m., and as on a horizontal path the velocity will not sink below 300 m., the law may be taken to hold throughout the trajectory.

H. B.

LIGHT.

131. *Double-movement Spectroscope Stand.* **F. L. O. Wadsworth.** (Zschr. Instrumk. 14. pp. 364-366, 1894.)—A new construction of spectroscope slit-frame, in which both plates are moveable and so arranged that the micrometer-screw sends them apart through equal distances, the result being that the centre of the slit remains in the same position. A spring prevents any part of the movement of this screw from becoming dead; so that measurements are rendered exact. The movement is between guides and the screws are centred, so that the slit remains parallel-sided whatever be its breadth. There is no risk of the slit-plates damaging each other through over-winding. A. D.

132. *Spectroscope.* **C. Pulfrich.** (Zschr. Instrumk. 14. pp. 354-363, 1894.)—The author, writing from Zeiss' works in Jena, describes a form of spectroscope in which the principle is applied of auto-collimation of refracted rays by their being made to turn back upon their own path upon encountering a silvered-face of a half-prism substituted for a whole prism of the usual series. Only half the usual number of prisms is then necessary. The advantages of the system, in spectroscopy, are the fixed position of the telescope-tube, the ease of manipulating for the angle of minimum deviation, the great focal length which it is possible to allow the telescope-combination, and the smaller number of reflections. The minimum deviation is attained by simple rotation of the combination round the first refracting surface, a method which enables measurements to be accurately made in terms of angles. The prisms used are Jena glass of great transparency: flint glass half-prism, refracting angle 57° , $n_D=1.6800$, $n_F-n_C=0.02152$, $\nu=31.6$; crown glass prism external, refr. ang. 40° , $n_D=1.5170$, $n_F-n_C=0.00847$, $\nu=61.0$; whence the dispersion for the region between C and F is $4^\circ 34'$, about three times that of an ordinary flint-glass prism of 60° . With $2\frac{1}{2}$ or $3\frac{1}{2}$ prisms, the dispersion can be greatly increased: and by the use of cinnamic ether in one of these prisms, the dispersion may be $12^\circ.1$. The instrument as constructed has much the form of an ordinary microscope with sloping tube: the observer looks down and turns a screw to secure minimum deviation. Focussing, scale, &c. are provided for, and stray light from reflecting surfaces is thrown far out of focus so as simply to dilute the field slightly. A. D.

133. *Spectroscope.* **J. Scheiner.** (Zschr. Instrumk. 14. pp. 316-324, 1894.)—In continuation of previous notes (Zschr. Instrumk. 1892, p. 365):—

The Spectroscope of Allegheny Observatory.—American spectroscopists seem to lean towards universal spectroscopes, which can be promptly adapted to various purposes. The German, especially

at Potsdam, lean towards separate instruments for separate purposes. By this moveable parts are reduced, mechanical strength may be increased, and also stability, which is so important in photographic and spectrometric work. The advantages of the American plan seem illusory: with so many removeable parts, there can be no stability; there is no great economy in cost, for the adapters are complicated and expensive, while each of the German instruments is simple; and the new testings and adjustments which must be made after each change waste much time. The Potsdam instruments all stand ready adjusted. The new Allegheny Observatory spectroscope (by Keeler and Brashear) is a universal spectroscope in the fullest sense of the term; it can be used for direct observation and for photographing, with diffraction-grating and with different prisms. Then follows the description from Keeler's paper in 'Astronomy and Astrophysics,' no. 111. Scheiner thinks the prisms may be firm enough in their seat as regards shaking, &c., but not quite so in respect of shifts caused by changes of temperature.

The Spectroheliograph.—Geo. E. Hale's description in *Astron. & Astroph.* no. 113, reproduced. The instrument moves a spectroscopic slit uniformly across the sun's apparent face, and along with this slit another moves parallel to it, immediately in front of the photographic plate, at such a rate as to allow only light of a uniform colour, present in the protuberances, preferably the line K, to reach the plate. The result is a photograph of the sun, done with monochromatic light only, and showing the chromosphere and protuberances, and maculæ all over the sun's disc. Adjustments are provided for obtaining an undistorted image.

The Edinburgh Royal Observatory Spectroscope.—Description by C. Becker, *Astron. & Astroph.* no. 116.

The Tulse Hill Spectroscope (W. Huggins, *A. & A.* no. 117).—It is interesting to see how the father of astrophysics endeavours to secure rigidity, even with some moveable parts. The star is very ingeniously put and kept in the slit by the aid of a total-reflection prism a little to one side of the telescope-rays. In this prism is seen, by means of an ocular, an image of the slit and of the stars reflected from its polished and somewhat inclined side-plates.

A. D.

134. *Interference Refractometer.* **L. Mach.** (*Zschr. Instrumk.* 14. pp. 279-283, 1894.)—Reference to the instrument described in *Anzeiger d. Wien. Akad.* and discussed, as to its theory and use, in *Sitzungsber. d. Wien. Akad.* 12. Oct. 1893. Practical details here given as to its working and as to recent improvements in the apparatus.

A. D.

135. *Colorimeter with Lummer-Brodhun Prisms.* **H. Krüss.** (*Zschr. Instrumk.* 14. pp. 283-285, 1894.)—Reference to the author's own four-prism instrument, described *Zschr. Instrumk.* 14. p. 102, March 1894, and to Pulfrich's two-prism instrument,

described *ibid.* p. 210, June 1894. Comparative diagrams are here given of the two instruments, and it is pointed out that though the four-prism instrument is at first sight much less symmetrical than the other, it secures equality of path in glass for the two rays compared, which the other does not, and also involves an equal number of reflections. The inequality of path in Pulfrich's instrument may lead to an aggregate error, through absorption, of about 7 per cent.; and through selective absorption may lead to colorimetric errors, for the computation of which the paper gives data. A. D.

136. *Telescope.* **K. Strehl.** (*Zschr. Instrumk.* 14. pp. 206–208, 1894.)—Instead of using (André) only the peripheral portion of a large lens, the author suggests the use of two diametrically-opposite sectors from a ring representing such a peripheral portion. Instead of these may be used two achromatic prisms, to bend the rays towards an axial crossing-point, and two lenses or pairs of lenses, to bring them to a focus at that point. The focal distance should not be greater than the distance between the two lenses. At right angles to the line joining the two sectors or prisms the resolving power is not greater than, but in the line joining them it is twice as great as, that of a large lens whose diameter is equal to the distance between the mid-points of the two objectives. The arrangement is better adapted for the resolution of double stars than for that of surface-details. A. D.

137. *Standard Wave-Lengths.* **A. A. Michelson.** (*J. Phys.* 3. pp. 5–22, 1894.)—In the author's Differential Refractometer, interference takes place between one ray directly transmitted through a plane parallel-sided plate of glass at 45° , reversed by a mirror M' , and reflected by the back of the plate to the eye; and another ray, part of the original beam, reflected from the first face of the plate, reversed by a mirror M'' , and transmitted through the plate to the eye. The light used is monochromatic, and by adjusting the respective positions of the mirrors, perfect optical contact of the real image of the ray from M' with the reflecting surface of the mirror M'' may be secured. As M'' is drawn back or fore, the interference-phenomena go through periodical changes. The result obtained is that the red cadmium line corresponds, at 15° C. and 76 cm. pressure, to 15,531.64 wave-lengths per centimetre. This line is one of the most simple and homogeneous in the spectrum: most of the well-known lines are complex: the hydrogen red line is double; each element of the sodium double-line is itself double or perhaps quadruple; the mercury green line is composed of five or six, of which the principal has two components, at a distance from each other equal to $0.002 \times$ the distance between the two sodium lines. A. D.

138. *Testing Quartz Plates.* **B. Brunhes.** (*J. Phys.* 3. pp. 22–28, 1894.)—A quartz plate is arranged at 45° between two crossed Nicols, each at 45° to the plane of incidence, and it is

turned in its own plane until darkness is restored in the second Nicol. The light reflected from it is passed, at right angles to the original direction, through an analyser, to be examined by a spectroscope. The polariser is then turned into the plane of incidence, and the analyser perpendicular to that plane. A channelled spectrum may then be observed. If the analyser and polariser be each turned through 90° , so as to reverse their relations to the plane of incidence, then, if the quartz be quite parallel-sided, the spectrum observed is unchanged; if it be not, the alternate bands shift in opposite directions. An error of $30''$ can be readily recognised in a quartz 1 mm. thick, and with thicker quartzes the sensitiveness is greater. A. D.

139. *Secondary Fringes in Newton's Rings.* **R. Boulouch.** (J. Phys. 3. pp. 28-31, 1894.)—The author discusses certain secondary fringes, due to multiple reflection and interference, and best seen by means of a lens below and a prism above. The lower face of the lens is silvered. The rays have then undergone two reflections in the air-layer and three at the silvered lens-face. The fringes are rectilinear and equidistant, with white centre, and are perpendicular to the plane of incidence; their distance is inversely proportional to the thickness of the lens; they close up as the angle of incidence increases, spread apart when it diminishes, and disappear at the normal incidence. A. D.

140. *Photography in Colours.* **G. Lippmann.** (J. Phys. 3. pp. 97-107, 1894.)—Deals mathematically with the reflecting power of the deposit obtained in his colour-photography process. The stationary vibration in the film results in a chemical action and in a consequent deposit of silver, which varies from nothing at the nodes to a maximum at the centre of the loops, or, in the case of compound light, is a function of the sum of the amplitudes. The light reflected by the prepared picture in the film is reflected, not from a surface, but from a thick film whose reflecting power varies with the depth; the reflecting particles may be considered as distributed according to the harmonic-function law in a homogeneous and unaltered medium; and the resultant is estimated by taking into account not only the variations of this reflecting power, but also the differences of phase occasioned by reflections from different depths below the external surface. In the case of a simple vibration in one plane being the cause of the original chemical action, the nodes are $\lambda/2$ apart; and if white light then shine upon the developed and dried plate, the resultant reflected light tends towards zero as the thickness of the film increases, except in the case of an incident light, or a component of the incident light, which has a wave-length λ or some sub-multiple of λ ; the practical case being (on account of the short range of visibility of the spectrum) that only in which the incident light has wave-length λ , the same as the wave-length of the light photographed. When the light photographed is heterogeneous,

the amplitude of the reflected light is the same as if each of the component original vibrations had acted separately; and the reflecting power of the developed plate for light of any wave-length λ' is determined entirely by the amplitude of light of that wave-length in the light photographed. Consequently, each component of incident white light is reflected by the developed plate in the same proportion as its components were present in the original light photographed; and the colour of the picture, as seen by reflection in white light, is the same as that of the object.

A. D.

141. *Composition of Light from various Sources.* **E. Köttgen.** (Wied. Ann. 53. pp. 793-811, 1894.)—Measurements with A. König's spectrophotometer of the composition of the light from a number of oil- and gas-lamps, and of cloud, sky, and sunlight. Tables and diagrams are given showing the distribution of intensity in the spectrum from $\lambda = 690 \mu$ to $\lambda = 430 \mu$, as compared with the distribution in a standard Hefner lamp.

R. A. L.

142. *A New Spectrophotometer.* **A. König.** (Wied. Ann. 53. pp. 785-792, 1894.)—For the production of monochromatic fields, König avails himself, in his physiological researches, almost exclusively of the method of Helmholtz & Maxwell, and he considers this method well suited for mere photometric comparisons. The photometer was first described in 1885, is manufactured by Schmidt and Hänsch, was tested and improved by Stössel and Wiedeburg in 1888, and has now again been studied by Miss Köttgen. If a prism is interposed between the collimator and the eyepiece, two slots, $s_1 s_2$, vertically above one another will produce two images, $\sigma_2 \sigma_1$. By adding a Rochon prism, each of the images is split into two, polarised at right angles to each other. If a twin prism, an obtuse isosceles triangle in cross section, is further interposed, we get twice four images, $\sigma' \sigma''$. The angle is chosen so that $\leftrightarrow \sigma'_2$ coincides with $\updownarrow \sigma''_1$; the arrows indicate the planes of polarisation; the other images do not concern us. The observer looks through a slot, a little shorter than the two spectra, towards the twin prism, whose two faces are illuminated by $s_1 s_2$. Owing to losses by reflection, the intensity of the two fields will not be the same, even if both s_1 and s_2 are illuminated by the same source. If now a Nicol is introduced and equal illumination secured, the intensities of the two sources of light, and the absorption-coefficient of the medium, can be deduced from the relative positions of the Nicol and the Rochon prisms. The author enters fully into the adjustment of the instrument, which requires very great care, but will be permanent provided no vertical pressure be exerted upon the tubes. The descriptive details he leaves to Miss Köttgen.

H. B.

143. *Dispersion of Fluorite, and Ketteler's Theory.* **F. Paschen.** (Wied. Ann. 53. pp. 812-822, 1894.)—The author, having measured the refractive index of fluor-spar for radiation, extending to $\lambda = 9.429 \mu$, compares the experimental numbers with the customary Briot's formula with four constants,

$$\frac{1}{n^2} = -dl^{-4} - bl^{-2} + a + cl^2,$$

where n = refractive index, and l = wave-length in the spar: the agreement is unsatisfactory, but becomes good by adding a term el^4 . To justify that, the author considers Ketteler's theoretical formula, with two absorption-bands, one in the ultra-violet, the other extending from $\lambda = 7$ downwards. In the region covered by observation, the absorption being small, the expression simplifies to

$$n^2 - a^2 = -\frac{M_1}{\lambda_1^2 - \lambda^2} + \frac{M_2}{\lambda^2 - \lambda_2^2},$$

where λ_1, λ_2 are the positions of the bands, and gives the required term. The latter formula with

$$\begin{aligned} a^2 &= 6.09104, & \lambda_1 &= 35.475 \mu, \\ M_1 &= 5099.15, & \lambda_2 &= 0.094256 \mu, \\ M_2 &= .00612093, \end{aligned}$$

gives close agreement from $\lambda = .18$ to $\lambda = 9$ R. A. L.

144. *Elliptically Polarised Electrical Rays and Electrical Resonance.* **L. Zehnder.** (Wied. Ann. 53. pp. 505-512, 1894.)—Two wire gratings are placed with their planes parallel, and with their wires parallel to the oscillator. The gratings are then rotated in their own planes through angles of 45° each, but in opposite senses. Then, of the waves incident upon the first grating, the component parallel to the wires is reflected while that perpendicular is transmitted. This component is parallel to the wires of the second grating, and is therefore reflected by it and freely retraverses the first grating on its return. We thus have, emerging from the first grating towards the oscillator, two sets of waves polarised in perpendicular planes and of approximately equal amplitudes. By adjustment of the distance between the gratings, these two rays are obtained with any desired phase-difference; while the ratio of the amplitudes of the components is controlled by the orientation of the wires of the gratings. Thus elliptically and circularly polarised rays may be produced at pleasure. The nature of the polarisation in each case is ascertained by a straight resonator capable of rotation about the direction of the ray as an axis. The second part of the paper continues the discussion between the author and Kr. Birkeland on electrical resonance as estimated by different methods. E. H. B.

145. *Alkaline Peroxides as Photographic Developers.* **G. A. Le Roy.** (C. R. 119. p. 557, 1894.)—Alkaline peroxides in aqueous solutions as well as oxygenated alkaline waters reduce

the silver haloids of gelatine plates, and the reduction is fairly proportional to the exposure. Longer exposure is needed, however, and the developer offers no advantages. The image, formed by metallic silver and oxides, loses in intensity in a hypo-sulphite or a sulphocyanide bath. H. B.

146. *The Degree of Incandescence of Lamps.* **A. Crova.** (C. R. 119. pp. 627-630, 1894.)—In order to determine the degree of incandescence, Crova examines the light through a solution of ferric and nickelous chlorides, which allow rays between 630 *d* and 534, principally those about 582, to pass, and further through red glass, comparing in both instances with the carcel. The first determination gives the luminous intensity, the second the degree of incandescence, both based upon the carcel as unit. This method, which he brought before the Electrical Congress of 1889, is said to answer well for comparison of different tints. The degree of incandescence of an arc lamp of 1500 or 1660 watts varies between 1·5 and 1·7; that of a 6-candle lamp between 1·05 and 1·23; that of a Bourbouze lamp with platinum netting increases with the gas consumption and reaches 1. Aner burners give the following results:—

Light	4·42	5·23	5·35 carcel.
Incandescence	1·30	1·41	1·47 „
Gas consumption per hour	93	105	102 litres.
„ „ per carcel.	21	20	19 „

Lamps which have a fixed quantity of glowing oxides should be pushed to full incandescence. In ordinary burners of the Bengel type there is no fixed quantity of incandescent material; the incandescence rises with the gas consumption, but at a diminished rate.

Light in carcels.	Gas-consumption in litres.	
	per hour.	per carcel.
0·2	56	280
0·4	78	195
0·6	95	158
0·8	108	135
1·0	120	120
1·2	131	109

Beyond 131 litres; the flame became sooty.

H. B.

HEAT.

147. *Thermodynamics of Capillarity in case of Continuous Variation of Density.* **J. D. van der Waals.** (Zschr. f. phys. Chem. 13. pp. 657-725, 1894. From Arch. Néerl. 28. pp. 121-209. Verhandel. d. K. Akad. v. Wetensch. te Amsterdam, Deel i. Nr. 8, 1894.)—Neglecting capillary effects and external forces, such as gravity, and therefore taking ϵ and η , the energy and entropy per unit mass at any point of a substance of mass m at constant temperature τ and occupying a constant volume k , to depend only on the density ρ or specific volume v at the point, we have for equilibrium

$$\int \rho dk = m \quad \text{and} \quad \int (\epsilon - \tau\eta) \rho dk \text{ a minimum:}$$

hence

$$\delta \int (\epsilon - \tau\eta - \mu) \rho dk = 0,$$

where μ is a constant, so that $\epsilon - \tau\eta + pv = \mu$ at every point and $vdp \equiv d(\epsilon - \tau\eta + pv - \mu) = 0$ or the pressure p , and consequently the density ρ , is constant throughout the volume; also

$$\delta^2 \int (\epsilon - \tau\eta - \mu) \rho dk > 0,$$

so that $\partial p / \partial v < 0$, and thus the isothermal on a pv -diagram must be convex toward the v -axis. This is for homogeneous distribution in stable phase; for volumes therefore for which the isothermal is concave to the v -axis there is instability and the substance splits up into two phases corresponding to points of tangency of the isothermal with a double tangent—even so too in general for the stable homogeneous states between these points, since, though $\epsilon - \tau\eta$ is for these a minimum, the sum of the values of $\epsilon - \tau\eta$ for the separated parts is still less and corresponds therefore to greater stability.

In the case of separation, however, the energy at a point may, in the separating layer at least, depend also on the variation of density in the neighbourhood. Suppose there is a continuous variation of density in parallel plane layers; then if ϵ_1 is the energy per unit mass in the middle of the substance, of density ρ_1 , in one of the phases, that at a distance h towards the substance in the other phase where the density is ρ is found to be

$$\epsilon = C - a\rho - \frac{1}{2}c\bar{d}^2\rho/dh^2 - \dots,$$

where

$$a = \int_0^\infty \psi(u) du, \quad c = \int_0^\infty u^2 \psi(u) du, \dots,$$

capillarity thus on this theory depending on c and not on Laplace's

$H \equiv \int_0^\infty u \psi(u) du$. The entropy at a point, however, probably depends only on the density at the point.

Then, neglecting $d^3\rho/dh^3$, . . . and putting

$$f(\rho) \equiv \epsilon - \tau\eta + \frac{1}{2}cd^2\rho/dh^2,$$

so that $\rho\partial f/\partial\rho = pv$ and $f(\rho) = -\int p d\rho$,

we have for equilibrium

$$\delta \int \{ f(\rho) - \frac{1}{2}cd^2\rho/dh^2 - \mu \} S \rho dh = 0,$$

where S is the constant area of the parallel layers, so that

$$f(\rho) + \rho\partial f/\partial\rho - cd^2\rho/dh^2 \equiv \epsilon - \tau\eta + pv - \frac{1}{2}cd^2\rho/dh^2 = \mu$$

at every point. Thus the thermodynamic potential $\epsilon - \tau\eta + pv$ is not constant throughout the volume, as assumed by Gibbs. Assuming that sufficiently far from the separating surface there is on each side homogeneous distribution of substance or $d^2\rho/dh^2 = 0$, we have

$$\epsilon_1 - \tau\eta_1 + p_1v_1 = \mu = \epsilon_2 - \tau\eta_2 + p_2v_2,$$

and furthermore $p_1 = p_2$, while in the limiting layer the distribution of density is given by

$$cd^2\rho/dh^2 = \partial/\partial\rho \cdot \rho \{ f(\rho) - \mu \}.$$

Examination of the last function shows that $d^2\rho/dh^2$ is 0 at the liquid end of the layer, becomes negative as the layer is entered, diminishes to a minimum and then rises to a positive maximum, finally becoming 0 at the vapour end of the layer, so that on a ρh -diagram the isothermal consists of two straight lines parallel to the h -axis joined without discontinuity by a curved line with one point of inflection. This distribution of density, which in free space would be unstable, is stable if

$$\delta^2 \int \{ f(\rho) - \frac{1}{2}cd^2\rho/dh^2 - \mu \} S \rho dh > 0,$$

and this the author shows to be in general true. Further, since

$$cd(d^2\rho/dh^2) = d\{ f(\rho) + pv - \mu \} = v dp,$$

the pressure in the layer is

$$p = p_1 + c\{ \rho d^2\rho/dh^2 - \frac{1}{2}(d\rho/dh)^2 \}.$$

And again, the function $\epsilon - \tau\eta + p_1v$ has a greater value at each point of the layer than elsewhere by

$$\epsilon' \equiv \epsilon - \tau\eta + p_1v - \mu = \frac{1}{2}c\{ v(d\rho/dh)^2 - d^2\rho/dh^2 \},$$

so that the whole layer has an excess of energy

$$\int \epsilon' S \rho dh = c S \int (d\rho/dh)^2 dh$$

or a surface-energy $\sigma \equiv c \int (d\rho/dh)^2 dh$:

but the value of ϵ' shows that only those parts of the layer which may be considered distended liquid contribute to its capillary energy, those which may be considered compressed vapour taking from it. In like manner, doubtless, may the surface-energy of a solid be diminished by gas condensed on it.

In the case of a sphere of liquid surrounded by vapour or of a spherical bubble of vapour enclosed in liquid, the equilibrium-condition is

$$f(\rho) + \rho \partial f / \partial \rho - c \{ d^2 \rho / dR^2 + 2(d\rho/dR)/R \} = \mu,$$

whence

$$p_1 - p_2 = 2c \int_{R_1}^{R_2} (d\rho/dR)^2 R^{-1} dR \simeq \pm 2\sigma/R$$

and also $p_1 - p_1' = 2\sigma\rho_1/(\rho_1 - \rho_2)R$,

which are known results, p_1' being the pressure with a plane surface.

The value of the capillary energy near the critical point, the thickness of the capillary layer, and its thermic properties are then investigated, and the theory is shown to yield the usual capillary formula on the assumption of discontinuity at the separating surface. Lastly the effect of taking $d^4\rho/dh^4$ into account with the special value $\psi(u) \equiv \exp(-\mu/\lambda)$ is considered, and five appendices discussing certain points at length are added.

R. E. B.

148. *High-Temperature Thermometers.* **A. Mahlke.** (Zschr. Instrumk. 14. pp. 73-79, 1894.)—High-temperature thermometers may be compared in a bath containing a mixture of potassium and sodium nitrates in a state of fusion, and the author describes a form of bath designed for this purpose. A correction must be applied to the readings of each thermometer, as the upper part of the mercury thread cannot be surrounded by the liquid, and this correction is determined by placing beside each an auxiliary thermometer having for its bulb a long capillary tube whose lower end dips into the liquid and whose upper end is near the reading-point of the thermometer under test. The results of a number of comparisons is given, showing differences which in the neighbourhood of 400° C. only very rarely reach three tenths of a degree.

L. R. W.

149. *The Determination of Absolute Temperature.* **L. Boltzmann.** (Wied. Ann. 53. pp. 948-954, 1894.)—From Thomson and Joule's experiments on the flow of gases Weinstein obtained a formula expressing absolute temperature T in terms of only the pressure, density, and empirical temperature t of a gas. This is not possible: for the heat required for a small change of condition may be written

$$dQ = AT \left(\frac{\partial p}{\partial t} \middle/ \frac{dT}{dt} \right) dv + \left\{ \psi(t) + AT \frac{\partial}{\partial t} \left(\frac{\partial w}{\partial t} \middle/ \frac{dT}{dt} \right) \right\} dt,$$

where w is the indefinite integral $\int p dv$ with t constant; so that either the latent heat of dilatation, or the constant-volume specific heat, or a similar magnitude must be known in addition to the

characteristic before T can be determined. The difference of the specific heats is, for instance,

$$\gamma_p - \gamma_v = -AT \left(\frac{\partial p}{\partial t} \right)^2 / \frac{\partial p}{\partial v} \left(\frac{dT}{dt} \right)^2,$$

whence
$$T^{\frac{1}{2}} = \frac{1}{2}A \int dt \frac{\partial p}{\partial t} / \left\{ (\gamma_v - \gamma_p) \frac{\partial p}{\partial v} \right\}^{\frac{1}{2}} + \text{const.}$$

Since the heat that must be given to a fluid to produce by a reversible process the same change of state as finally occurs when the fluid expands irreversibly without doing work or receiving heat is equivalent to the work done in that process, the irreversible changes of v and t are connected by the relation

$$Ap dv = AT \left(\frac{\partial p}{\partial t} / \frac{dT}{dt} \right) dv + \gamma_v dt,$$

whence the equation to be used with the T . and J . experiments is

$$\left(p - \gamma_p \frac{dt}{dv} / A \right) \left(\frac{dT}{dt} \right)^2 - T \frac{\partial p}{\partial t} \frac{dT}{dt} - T \frac{dt}{dv} \left(\frac{\partial p}{\partial t} \right)^2 / \left(\frac{\partial p}{\partial v} \right) = 0.$$

[In the memoir a misprint occurs in the value of dQ , and a slip in that of $\gamma_p - \gamma_v$, so that the integral and the last equation are not the same as above.]

R. E. B.

150. *High-Temperature Mercury Thermometers.* **A. Mahlke.** (Wied. Ann. 53. pp. 965-999, 1894.)—The work of reducing mercury thermometers made of Jena glass No. 59^{III} to the air thermometer between 300° and 500° C. was carried on at the Physikalisch-Technische Reichsanstalt in order to standardise the high-temperature thermometers already constructed of that material. These thermometers, which are used considerably above the normal boiling-point of mercury, are prepared by filling the upper part of the capillary with carbonic acid under pressure. In order to study the apparent expansion of the mercury under pressure, special thermometers are constructed provided with two large bulbs at the top, both containing compressed CO₂. One of these was attached to the capillary by means of a tube at right angles to it, provided with a bulge into which a portion of the mercury thread can be led by cooling the CO₂ in the bulb. As a result of an elaborate series of experiments, the following are given as the indications of a mercury thermometer of this kind under 8 atmospheres' pressure, the scale being continued from that between 0° and 100°:—

Air therm. ...	100	300	325	350	375	400	425	450	475	500
Mercury „ ...	100	304.1	330.9	358.1	385.4	412.3	440.7	469.1	478.0	527.8

E. E. F.

151. *Direct Experimental Determination of the Specific Heat of Saturated Vapour and of the Internal Heat of Vaporisation.* **E. Mathias.** (C. R. 119. pp. 849-852, 1894.)—This method presumes a knowledge of the relations connecting the pressure f and density $1/u'$ of saturated vapour, as also the specific heat s and density $1/u$ of saturated liquid, with the temperature t and also of the internal heat of vaporisation ρ at normal temperature and the specific heat z of the superheated vapour. A vessel, of water-equivalent M , in which is placed the mass P of liquid which is calculated to fill it as saturated vapour at t , is kept for some hours at a fraction ϵ of a degree above t and then plunged into a calorimeter. The final temperature being θ , the heat given up q , and the mass of vapour condensed p ,

$$q - M(t + \epsilon - \theta) - Pze$$

measures the change of energy of p saturated liquid and $P - p$ saturated vapour at θ in becoming P saturated vapour at t . This being expressible as

$$p\rho + P \int_{\theta}^t s' dt - \mathfrak{A}P \int_{\theta}^t f du,$$

where \mathfrak{A} is the heat-equivalent of work and s' the specific heat sought, we have at once $\int_{\theta}^t s' dt$ and ρ' , the internal heat of vaporisation, since

$$\rho' = \rho - \int_{\theta}^t \{ (s - s') dt + \mathfrak{A} f d(u' - u) \};$$

and s' is graphically deduced from the curve obtained by plotting the values of $\int_{\theta}^t s' dt$, where θ has a constant value. The results of 11 experiments on sulphurous acid are given, and certain deductions are drawn as to the representative curve [which do not however seem to be justified by the numbers given.] **R. E. B.**

152. *Present State of High-Temperature Research.* **Carl Barus.** (Am. J. Sc. 48. pp. 332-336, Oct. 1894.)—The author shows that to clear away the anomalies now existing in high-temperature data either the reputed boiling-point of zinc must come down from 930° to 905° , or else the reputed melting-points of silver, gold, and copper must move up 30° to 40° , or both must move each towards the other by corresponding amounts. **E. E. F.**

153. *Theory of Liquids and Gases.*—II. **G. Bakker.** (Zschr. phys. Chem. 14. pp. 446-455, 1894.)—A mathematical investigation of the molecular pressure in fluids on the principles of thermodynamics. **W. C. D. W.**

154. *Thermodynamical Proof of Van der Waals' Equation for Liquids and Gases.* **G. Bakker.** (Zschr. phys. Chem. 14.

pp. 456-466, 1894.)—Three assumptions are made. (1) that however high the temperature may be the variations from the laws of Boyle and Gay-Lussac are always finite; (2) that two elements of fluid attract each other with a force which, for a given temperature, depends only on their masses and the distance between them, and falls off quickly as the distance increases; (3) that the kinetic energy is a function of the temperature. The author then shows, by the methods of the last paper, that on these assumptions the most general form of equation to express the state of the substance is

$$p = \frac{RT}{v-b} - \frac{a}{v^2},$$

where b can be a function of the volume, which becomes constant or zero at great dilution. When a change in the state of molecular aggregation occurs, the second assumption probably ceases to hold good, and the equation must be written

$$p = \frac{RT}{v-b} - \frac{a_0 f\left(\frac{T}{T_k}\right)}{v^\mu},$$

where T_k is the critical temperature and b , a_0 , and μ are constants.

W. C. D. W.

ELECTRICITY.

155. *Theory of Capillary Electrometer.* **K. Schreber.** (Wied. Ann. 53. pp. 109-134, 1894.)—According to Helmholtz,

$$\frac{\partial T}{\partial \phi} + \epsilon = 0,$$

where T is the surface-tension of a mercury-electrolyte surface, ϕ the potential-difference between the liquids, and ϵ the electric surface-density. The author made experiments with a ballistic galvanometer in circuit with a capillary electrometer to find the relation between ϕ and ϵ in order to integrate the equation. He also works out a theory of the phenomenon based on the osmotic pressure of the ions near the surface. He finds from theory and experiment,

$$\frac{\partial T}{\partial \phi} + A\phi\rho_B\phi = 0,$$

disagreeing with Lippmann's assumption that $\frac{d^2T}{d\phi^2} = -c$, or that the capacity of the surface is constant. The natural potential-difference of mercury and dilute sulphuric acid is .95 volt.

R. A. L.

156. *An Electro-chemical Method of recording Alternating Currents.* **P. Janet.** (J. de Phys. 3. pp. 455-459, 1894.)—A metal cylinder is wrapped with paper which has been soaked in a solution of potassium ferrocyanide and ammonium nitrate (equal parts of saturated solutions and six of water), as employed in Bain's electro-chemical telegraph. An iron or steel stylus lightly touches the surface of the paper. The cylinder and stylus are connected to two points between which is an alternating pressure; on rapidly rotating the cylinder, each time that the excess of potential of the point above that of the cylinder reaches a certain positive value a blue trace is left on the paper, and there being no self-induction in the cylinder branch, these traces will be in step with the pressure producing them, and the number of marks will correspond to the number of periods. By arranging another stylus side by side with the former one, a clock or pendulum can be made to give marks every second. To obtain the frequency it suffices to count the number of marks existing between two successive marks due to the clock. By means of this method the author has studied and obtained graphical records of differences of step between two currents in a non-inductive and an inductive resistance in parallel with one another, and in other cases. Two styluses are employed; and as two pressures between three points are required, the middle point is connected to the cylinder and the two others each to a stylus. Obviously, if there be no difference

of step between the pressures, the marks in one trace will come between those in the other, and any difference in step will set back one set of marks behind their proper position, and from the amount of setting back the author proposes to determine the difference in step. Of course in the case of the current in the inductive resistance, the pressure must be taken between the terminals of a non-inductive resistance in series with it. Finally by the use of three styluses the author has applied the method to show the step-differences in the case of triple E.M.F.'s, when he obtains three lines of marks displaced with regard to one another by one third of a period.

E. C. R.

157. *Researches on Stationary Electric Waves.* **E. Salvioni.** (Nuov. Cim. 34. pp. 155-180, 1894.)—The problem discussed in this paper is that of obtaining a formula giving the wave-lengths of the systems in a Lecher wire combination when the geometrical configuration is given. The constants entering into the formula obtained are the lengths of the primary and secondary wires, their distance apart, their radius, the capacity of the two condensers separating the primary and secondary circuits, and the capacity of the terminal condenser. The formula is somewhat complicated, but agrees very well with the observations. It was found that the nodes determined with the aid of a single bridge do not coincide with those determined with two bridges. The internodes increase towards the primary circuit, and these inequalities are due to the action of the bridge itself. When the length of the primary circuit is great in comparison with the internode, experiment reveals some wave-lengths which are not given by calculation. In this case there are some nodes in the primary circuit itself, as may be shown by substituting a condenser for the conducting bridge. For all wave-systems there is always a node where the exciter-spark crosses; the primary circuit must therefore be considered as closed by the spark.

E. E. F¹

158. *Resistance to a Spreading Current and Polarisation of Small Electrodes.* **K. R. Koch** and **A. Wüllner.** (Wied. Ann. 52. pp. 691-699, 1894.)—In a former paper (Wied. Ann. 1892, 45. p. 475) the authors found that their observations on the high polarisation of small electrodes could be represented as the sum of two terms, (1) the constant opposing electromotive force of the true polarisation (π), and (2) the product of a resistance (u) and the current (i), so that $p = \pi + iu$. Richarz (Wied. Ann. 1892, 47. p. 567) suggested that the whole phenomenon could be explained without supposing the existence of a special resistance at the junction, by the usual formula for calculating the resistance of the layers of a badly-conducting medium just outside a small electrode. The authors now use little circular electrodes, made by sealing platinum wires into glass tubes and cutting both off, so that the end of the wire is level with the glass. The resistance (w_a) of the

layers of neighbouring liquid through which the current spreading from each of these must pass, can be calculated when the specific resistance is known. The values of $\pi = \rho - 2i\omega a$ are tabulated for acid solutions of various concentrations, and show increases as the currents get larger, in one case from 5 to 53 volts. The authors therefore conclude that the spreading resistance is not in itself sufficient to explain the high polarisation, but that there must be another special resistance at the surface of the electrodes the nature of which is doubtful.

W. C. D. W.

159. *Oscillations of long duration.* **H. Ebert.** (Wied. Ann. 53. pp. 144-161, 1894.)—Two knobs, between which sparks are made to pass by an electrical machine, are each connected to one plate of two similar air-condensers, while the disengaged plates are connected by a coil of wire. Another similar coil wound together with the first has its ends connected with the plates of a third air-condenser. The electric oscillations set up in the first coil produce by mutual induction oscillations in the second, and the distances of the condenser-plates are adjusted so that the periods of free oscillations shall be the same for both coils. In this manner oscillations of definite period and with small dampings are obtained. A simple form of apparatus is described in which the above arrangement, among others, can be employed, and the period and intensity of the oscillations can be separately varied. The author has used this apparatus in studying the appearances presented when oscillatory discharges pass through rarefied gases. He has also shown that the relative brightness of the lines in the spectrum of such a gas, rendered luminous by an oscillatory discharge, varies with the period of the oscillations. Since considerable luminosity, unaccompanied by perceptible rise of temperature, is produced by the passage of such long-continued oscillations through a gas, they lend themselves to spectroscopic researches on substances whose decomposition or dissociation must be guarded against, and the author has employed them in obtaining the emission spectra of the undissociated molecules of bromine and of iodine, which he has described. He has also, by concentrating upon a phosphorescent substance the negative rays produced by such oscillatory discharges, obtained a lamp in which the light emitted bears an unusually great ratio to the energy supplied.

L. R. W.

160. *Capillary Electrometers and Drop Electrodes.* **G. Meyer.** (Wied. Ann. 53. pp. 845-873, 1894.)—The surface-tension of mercury and some amalgams with respect to saline solutions is diminished by the addition of a salt of mercury or of the metal contained in the amalgam, whilst that of other amalgams is not changed. The surface-tension curve observed with the capillary electrometer has an ascending branch when the mercury or the amalgams, whose capillary constants have been thus reduced, are kathodically polarised. The difference of potential between

two drop electrodes varies with the chemical constitution of the electrolyte into which they play, a relation which is not indicated by the accepted views regarding contact E.M.F.'s. E. E. F.

161. *Thermoelectricity of Chemically Pure Metals.* **K. Noll.** (Wied. Ann. 53. pp. 874-911, 1894.)—Very pure Pb, Zn, Sn, Cd, Bi, and Sb were obtained from Merck, Darmstadt, and pure Pt, Ag, and Au from Heräus, Hanau. The thermoelectric forces of the above and other metals were determined for the temperature-interval 0° – 100° , the metals being combined with mercury. The paper contains a table of these to hundredths of a microvolt. The metals were also combined among themselves at temperatures up to 217° . It was found that Avenarius' formula is valid for most of the combinations. The thermoelectric forces of the metals for 50° , referred to lead, are given below in microvolts:—

Cadmium	+4.71	Aluminium	— 0.41
Zinc	+3.318	Magnesium	— 0.113
Silver	+2.68	Iron	+11.835
Gold	+3.10	German Silver ..	—14.68
Copper	+3.22	Nickel	—20.58
Tin	—0.067	Mercury	— 4.03

E. E. F.

162. *Atmospheric Electricity.* **V. Dvorák.** (Zschr. phys. Chem. Unterr. 7. pp. 166-176, 1894.)—The measurement of atmospheric potential by the flame and electrometer method may be illustrated by means of a board carrying a piece of tinfoil 1 m. square, representing the earth's surface, and connected with one coating of a charged Leyden jar. A very small metal spirit-lamp connected with an electrometer and held above the surface will produce a deflection varying directly as the height above the surface, for short distances. A striking demonstration of the electrification of the air in the room may be given by connecting a spirit-lamp with one pole of an influence-machine and working the latter for a few minutes. The machine is then removed, and the electrification of the air demonstrated by means of a candle stuck on a needle mounted on an insulating stand, the needle being connected with an electroscope. E. E. F.

163. *A modified Wimshurst Machine.* **P. V. Schaffers.** (C. R. 119. pp. 535-537, 1894.)—The author states that the output of a Wimshurst Machine can be about doubled by modifying it as follows:—The plates are the same as in an ordinary Wimshurst; before one of them are mounted two straight insulated combs, before the other two combs making an angle of about 60° with the direction of the first. The two combs to the left are connected to one electrode, those to the right to the other. All

four combs are provided with rubbing brushes. Lastly, at 30° to 35° from the combs, in the direction of rotation of each plate, is a diametrical conductor having points without brushes. E. C. R.

164. *Change of Period of Electrical Waves on Iron Wires.* **J. Trowbridge.** (Amer. J. Sc. 48. pp. 307-310, Oct. 1894.)
Wave-Lengths on Iron Wires. **C. E. St. John.** (*Ibid.* pp. 311-325.) (Phil. Mag. 38. pp. 425-445, Nov. 1894.)—Both these papers deal with the question whether the magnetic properties of iron are called into play under extremely rapid alternations of the magnetising forces, and the results of both, though obtained by entirely different methods, answer this question in the affirmative. Prof. Trowbridge discharged a Leyden jar through iron and copper wires respectively, taking care that the circuits had the same geometrical form in each case, and the resulting sparks, spread out by a revolving mirror, were photographed. The times of oscillation were in each case referred to a standard "time-circuit," so as to eliminate the errors due to changes in the angular velocity of the mirror. The most marked changes in period were obtained with iron wires 0.0312 in. in diameter. With distances on the "time-circuit" between two successive serrations on the photographic record of 6.08 mm. and 6.14 mm. respectively, the distance for the iron wire was 3.7 mm. and that for the copper 3.5 mm. These and many similar results show that the time of oscillation on an iron circuit is longer than on a similar copper circuit. St. John measured the wave-lengths in a simplified Lecher wire system consisting of copper or iron wires. It was found that in wires of the same diameter the wave-length in iron was from 1.5 to 2.0 per cent. shorter than in copper. The self-induction of iron circuits under oscillations with 115×10^6 reversals per second was 3 or 4 per cent. greater than that of similar copper circuits. The permeability of iron under this rate of alternation was about 385. E. E. F.

165. *Resonance Analysis of Alternating Currents.* **M. I. Pupin.** (Am. J. Sc. 48. pp. 379-389 and 473-485, Nov. and Dec. 1894.)—The presence of upper harmonics in an alternating current wave may be detected by a resonance method which is simpler and more sensitive than Joubert's sliding-contact method. An air-core transformer is inserted in the circuit of the alternator. The "resonant circuit" contains the secondary of the transformer, a rheostat, a mica condenser, and an inertia coil with a large number of turns of copper wire of low resistance, but containing no iron. In shunt to the condenser is an electrostatic multicellular voltmeter. The capacity of the condenser is gradually increased from zero upwards. Whenever a capacity has been reached which with the self-induction of the resonant circuit produces resonance with one of the harmonics in the main circuit, the rise of potential produces a large deflection in the voltmeter. The distortion of the primary current from various causes is studied in this manner. Thus it

is found that an iron cored coil in circuit with an alternator which gives a simple harmonic E.M.F. distorts the current by introducing higher odd harmonics, principally the harmonic of three times the frequency of the fundamental. When a transformer of the induction-coil type, with a cylindrical iron core made up of very carefully insulated fine iron wire, was put in circuit with the alternator, it was found that high degrees of magnetisation of the transformer core produce a strong deformation of the primary current wave. With inductions of over 12,000 it was possible to make the amplitude of the first odd harmonic even greater than the amplitude of the fundamental. E. E. F.

166. *Thermoelectric Properties of Platinoid and Manganin.* **B. O. Peirce.** (Am. J. Sc. pp. 302-306, Oct. 1894.) The following are some of the results obtained with platinoid and manganin wires of various diameters (American Gauge). The E.M.F.'s are given when the temperatures of the junctions were 0° and 100° C. respectively :—

	Microvolts.
Mercury vs. manganin No. 18	797
Mercury vs. platinoid No. 19	1331
Copper vs. manganin No. 18	64.9
Copper vs. platinoid No. 19	2063
Copper vs. platinoid No. 28	1787
Copper vs. manganin No. 22	257
Copper vs. ord. annealed manganin ..	180

E. E. F.

167. *Nodal Systems of Electric Waves obtained by Lecher's Method.* **D. Mazzotto.** (N. Cim. 36. pp. 189-207, Oct. 1894.)—This paper contains the results obtained in an investigation of the various wave systems produced in a Lecher wire system on varying the lengths of the primary and secondary wires and the distance apart of the plates of the condenser. A graphic method is given for obtaining all the possible systems for any given length of the secondary wires, when those corresponding to one length have been determined. Curves called "nodal lines" were drawn, with lengths along the secondary wires as abscissæ and distances of the second node from the condensers as ordinates. These were determined by placing the second bridge in a certain position and shifting the first bridge until the "explorer" placed midway between them showed a maximum effect, which diminished uniformly towards either of the bridges. This showed that the bridges were at the first two nodes of the wave system. The second bridge was then shifted towards the condensers and the process repeated, in order to obtain two more points in the nodal lines, and so on, until the bridges were inconveniently near the condensers. The bridges were then shifted outwards by the amount of one wave-length, and a repetition of the same process made the second bridge indicate the third nodal

line. By counting the wave-lengths backwards across the condenser *virtual* nodal lines were also constructed. These are wavy in the portions near the condenser, whereas the actual nodal lines continually recede from the axis of ordinates. This is due to the influence of the condensers, which is a maximum when a node of the secondary wires is at a distance from the condensers equal to the length of the primary wires. E. E. F.

168. *Relation between the Dielectric Constants and the Chemical Constitutions of Dielectrics.* **C. B. Thwing.** (Zschr. phys. Chem. 14. pp. 286-300, 1894.)—Measurements are made by a method depending on the resonance of electric vibrations. The period of vibration of an electrical system depends on its capacity and self-induction, so that if the self-inductions of two systems are the same, they must have the same capacity in order to keep in resonance with a third system. The capacity of an adjustable air-condenser was made equal to that containing the substance under investigation, and then its value calculated. Numbers are given for many solids and liquids, from which the following are selected:—

Paraffin	2.14	Propyl alcohol	20.45
Ebonite	2.71	Isopropyl alcohol	19.82
Glass	5.84	Formic acid	62.00
Ice (at -2°)	3.36	Acetic acid	10.30
Ice (at -5°)	2.85	Propionic acid	5.50
Water	75.50	Turpentine	2.28
Glycerine	56.20	Nitrobenzene	32.19
Methyl alcohol	34.05	Ethyl ether	4.27
Ethyl alcohol	25.02	Chloroform	3.95

Values are then given for mixtures of alcohol and water and other pairs of liquids, in varying proportions. The influence of temperature is investigated for the case of water, a maximum of 85.2 being found at 4° . The dielectric constant in many compounds seems to be an additive property, and can be calculated from constant values for their constituent atoms and groups, *e. g.*:—

$$K_H = 2.6, \quad K_C = 2.6 \times 12, \quad K_O = 2.6 \times 16, \quad K_{OH} = 1356, \\ K_{NO_2} = 3090, \quad K_{CH_2} = 41.6, \quad \&c.$$

In many cases the dielectric constant seems to be 2.6 times the density. W. C. D. W.

169. *Electrolytic Decomposition of Water.* **M. Le Blanc.** (Zschr. phys. Chem. 13. pp. 163-173, 1894.)—The author considers that the electrolytic decomposition of water is a primary, and not a secondary process, the addition of a salt serving to increase its capability to form ions. Its action with potassium shows that water contains electrolytic ions. Other evidence is given in favour of the theory of primary decomposition, which is more simple than that usually accepted. W. C. D. W.

170. *Fundamental Law of Electrolysis.* **O. Wiedeburg.** (Zschr. phys. Chem. 14. pp. 174-184, 1894.)—When the products of electrolysis are gaseous, von Helmholtz has shown that the relation between the electromotive force A and the pressure of the gas is given by $A_1 - A_2 = \text{const.} \log \frac{p_1}{p_2}$. The author therefore concludes that even the smallest electromotive force will produce a certain amount of electrolytic action. The curve showing the relation between electromotive force and current consists of two nearly straight portions connected by a short curved part at the position of maximum polarisation. W. C. D. W.

171. *Continuous Electrical Conductivity of Gases.* **F. Braun.** (Zschr. phys. Chem. 13. pp. 155-162, 1894.)—Mixtures of nitric oxide and air and of chlorine and hydrogen did not conduct at the moment of combination even when subjected to an E.M.F. of 4000 volts. A mixture of carbonic oxide and oxygen allowed a current of from 7 to 20 small Grove's cells to pass at the moment of explosion. When heated to 1000° or 1200° and a Leclanché cell applied, a Thomson's galvanometer showed the following readings:—

Iodine	20 to 30 scale-divisions.
CO ₂	0
H ₂ O	0
NH ₄ Cl	500 or more
HCl with air	20
NH ₃ with air	50
HI with some I	6
HBr	7
HgO	1.5 (?)
CdI ₂	400

The author considers the charges of flames to be due to a separation of ions. W. C. D. W.

172. *Change in the Conductivity of a Solution on Addition of a Small Quantity of a Non-Conductor.* **N. Strindberg.** (Zschr. phys. Chem. 14. pp. 161-162, 1894.)—An investigation by R. J. Holland (Wied. Ann. 50. p. 261) established the general accuracy of Arrhenius' formula $l = l_0 \left(1 - \frac{av}{2}\right)^2$ (in which l denotes the conductivity after the addition of x volumes per cent. of the non-conductor, and l_0 the conductivity before the addition), but gave different values for the coefficient a . The author has measured by Kohlrausch's method the conductivity of aqueous solutions of sodium and copper chlorides, to which varying amounts of redistilled ethyl alcohol or acetone were added, and finds numbers in accordance with Arrhenius' values. Some measurements made by Lenz give similar results. W. C. D. W.

173. *Estimation of Transition-points by an Electrical Method and the Electromotive Force of Chemical Combination.* **E. Cohen.** (Zschr. phys. Chem. 14. pp. 53-92, 1894.)—The temperature at which such an action as $\text{ZnSO}_4, 7 \text{H}_2\text{O} = \text{ZnSO}_4, 6 \text{H}_2\text{O} + \text{H}_2\text{O}$ takes place is determined by an electrical method. Saturated solutions of the two forms of the compound are placed one in each of two glass vessels and connected together by a moistened thread of wool. A rod of amalgamated zinc is placed in each vessel, and any difference of potential between them used to send a current through a galvanometer. As the apparatus is heated a current flows, which is reversed when the temperature of transition is reached. The method was also used in the case of the formation of double salts. A short thermodynamical account of such cells follows, based on the method of Gibbs and von Helmholtz. W. C. D. W.

174. *Transition Cells and a New Method of using them.* **E. Cohen and G. Bredig.** (Zschr. phys. Chem. 14. pp. 535-547, 1894.)—Cohen's method (see above) sometimes fails by reason of the supercooling of one of the saturated solutions. One electrode can then be immersed in an unsaturated solution, and a curve drawn between temperature and electromotive force. At the transition-point a sudden change in the direction of the curve is seen. Thus three cells containing saturated sodium sulphate solutions in one limb, and normal, $\frac{1}{2}$ normal, and $\frac{1}{4}$ normal solutions in the other, gave as the temperatures of transition from $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ to $\text{Na}_2\text{SO}_4 + 10 \text{H}_2\text{O}$, $33^\circ.8$, $33^\circ.0$, and $32^\circ.9$ respectively, numbers which agree well with Cohen's previous result, $32^\circ.8$. The connection between the results of this method and those obtained by the use of two saturated solutions is investigated thermodynamically and confirmed by experiment. W. C. D. W.

175. *Double-bifilar Electrometer.* **A. H. Borgesius.** (Zschr. Instrumk. 14. pp. 438-444, 1894.)—A circular metal disc surrounded by a guard-ring is suspended horizontally by a pair of bifilars. A second disc, below the first, forms a condensing system with it. If the suspended disc, before charging, is orientated, by a suitably applied couple, so that it takes a new position of equilibrium, the attractive force between the discs, when charged, can be measured by observing the angle through which the suspended disc moves from the uncharged position. Further, by adding known weights to the suspended disc, the instrument can be calibrated, and, from the equations of equilibrium, the electrical forces corresponding to given angles of orientation may be determined in absolute measure. The author applies the mechanical couple by a second pair of bifilars carrying a light aluminium ring which floats just above the disc; wires stretched diametrically across this ring come into gear with the bifilars supporting the disc, so that, by rotation at the bifilar-head, any required orientation of the disc can be made. A mirror is attached to a small bridge fixed across the top of the suspended ring. The sensitiveness

of the instrument can be varied conveniently by adding weights to the suspended disc; a hook and lever is provided for facilitating this operation. In its present form this electrometer does not appear to have been used for small potential differences; its purpose seems rather to measure volts of the order 1000-50,000.

R. A.

176. *Magnetic Measurements.* **A. Koepsel.** (Zschr. Instrumk. 14. pp. 391-397, 1894.)—The apparatus here described is intended for direct magnetic tests of samples of iron. In its original form the instrument consisted of two bobbins placed with their ends facing each other, with a suspended coil between them, supported by a torsion-spring. A steady current was maintained in the suspended coil. The samples of iron were inserted as cores within the bobbins, the consequent torsion-angles being taken as proportional to the respective fields. The improvements relate to the use of a yoke-piece completing the magnetic circuit of the samples, while retaining the method of measurement by torsion-coil. Experiments are made to determine the best position in the magnetic circuit for the necessary air-gap, so as to have minimum leakage of induction. These preliminary tests were by ballistic method. A gap in the samples themselves is found to be entirely unsuitable: gaps through the yoke give far better results, as might have been predicted from the relative sectional areas; but, even with a yoke-section many times greater than the section of the sample, there is a marked difference in the curves obtained respectively with and without air-gaps—the magnetising bobbins and the sample cores being entirely within the yoke. A gap of 5 mm. is broad enough for the insertion of a flatly wound torsion-coil. To increase the rotation-moment of the coil without enlarging the air-gap, a specially formed coil is inserted within a cylindrical annular air-space in the yoke, which is bored out for the purpose. This annular space was only 1 mm. across. Compensating-coils are wound outside the yoke, to neutralise the field due to the magnetising bobbins when no sample is in the apparatus. Careful ballistic measurements are made to calibrate the instrument, which is intended for use by unskilled hands, as a torsion-coil magnetometer.

R. A.

177. *Electrochemical Researches.* **A. Voigt.** (Elektrochem. Zschr. 1. pp. 161-163, 1894.)—Solutions of aniline, nitrobenzene, and other similar substances in various solvents, such as sulphuric acid, acetic acid, potash, water, and alcohol, either pure or mixed together, are placed in a porous cell, together with a platinum, carbon, or zinc plate, which forms the anode of the circuit of a battery consisting of a few Bunsen's or Daniell's cells. After different times, varying from half-an-hour to twenty-four hours, the products of the electrolysis are examined chemically, and thus the influences of the nature of the solvent and of the material

of the electrode are determined. The aniline solutions in acetic acid give several oxidation products, such as aniline-black, acetanilide, and amidohydroquinone. Nitrobenzene can be partly reduced to aniline, and bye-products, often vividly coloured, are also formed. Complete reduction cannot be obtained even in solvents like alcoholic potash, which are themselves reducing agents. The solvents are often attacked, and the complicated bodies produced disturb the course of the principal reaction.

W. C. D. W.

178. *Force acting at the Surface of Separation of two Dielectrics.* **H. Pellat.** (C. R. 119. pp. 675-678, 1894.)—The author imagines an air-condenser, between the vertical plates of which is a slab consisting of two halves of different dielectric substances, so arranged that the surface of separation between the halves is horizontal. By considering the change in the capacity of this system produced by raising the slab through a small distance, the force acting at the surface of separation is calculated. In a similar manner the author promises a general investigation of the force on the surface between two dielectrics in an electric field, which shall give all the usual results independently of any hypothesis.

W. C. D. W.

179. *Electric Arc.* **L. Thomas.** (C. R. 119. pp. 728-730, 1894.)—Having observed that the light from a region of the electric arc near the negative carbon is due to incandescent sodium vapour, the author made spectrophotographic observations on the light of various points in the arc. He finds that carbons containing metallic salts, and placed at a moderate distance apart, give a core of light due to carbon vapour and carbides, with an envelope, in which metallic vapours pass from the positive to the negative side; the metallic vapours burn off at the negative pole. The author concludes that the elements of air are carried to the positive pole, helping to disintegrate and heat it, and that the current is conveyed electrolytically by the metallic vapours, which serve also to protect the negative carbon from being attacked.

R. A. L.

180. *Propagation of Electromagnetic Waves in Ice, and Specific Inductive Capacity of this Body.* **R. Blondlot.** (C. R. 119. pp. 595-597, 1894.)—This is an account of some experiments made with a view of testing whether the law, which the author had given in a previous paper (C. R., 25 July, 1892), namely, that the wave-length of the radiation emitted by a given oscillator is independent of the nature of the insulating medium in which the oscillator is placed, held in the case when ice was the dielectric. The above law had been previously tested for turpentine and castor-oil, and the object in using ice was to see whether, in this extreme case, ice having (according to Bouty) a specific inductive

capacity of 78, the law was valid. The apparatus was the same as the author employed in the case of turpentine and castor-oil (see C. R. *loc. cit.*), a Lecher wire system being used. Four concordant experiments were made, which showed the above law to hold in the case of ice. From the numbers obtained it was possible to calculate the specific inductive capacity of ice, and the value obtained was $K=2$. The author considers this value for K to be correct to within $\frac{1}{20}$. W. W.

181. *Specific Inductive Capacity of Ice.* **A. Perrot.** (C. R. 119. p. 601, 1894.)—The author, having been informed of the value obtained by Blondlot for the specific inductive capacity of ice (see previous note), has revised the calculations used in reducing his results, which were published in the C. R., 27 June, 1892. From these former results and from some new experiments the mean value $K=2.04$ is obtained. W. W.

182. *Mean Values of the Magnetic Elements for the Earth and Lines of Equal Disturbance.* **A. de Tillo.** (C. R. 119. pp. 597–599, 1894.)—The author, making use of the maps published by Erman-Petersen, Sabine, Creak, and Neumayer, has calculated the mean value of the declination and dip, together with the horizontal and vertical components and the total intensity of the earth's field for the parallels of latitude. The values are given for four epochs, namely 1829, 1842, 1880, and 1885. For each element the values obtained at the different epochs for any given parallel are fairly constant, and thus, the author considers, they represent the permanent magnetism of the globe. The author has also drawn maps of the lines of equal disturbance for the declination, force, and magnetic potential, and finds that for each element the globe may be divided into two hemispheres by lines running from N. to S., such that for any one element the values in one hemisphere are, on the whole, greater than in the other. A connection is also evident between the directions of the lines of equal disturbance for the different elements. W. W.

183. *Photographic Recorder for Magnetometers and Galvanometers.* **K. Schering and C. Zeissig.** (Wied. Ann. 53. pp. 1039–1052, 1894.)—The new apparatus photographs the time, minutes and seconds, not the hours; at 31 min. 27 secs. the needle pointed to division 490.30". Each of the little photographs, which are taken at intervals of 10 seconds, is 1 mm. long, 1.5 mm. wide, so that, with 0.1 mm. blank space, 50 photographs would cover an area of 1 sq. cm.; the 150 photographs shown are on a plate 39 × 8 mm. The scale, 26" of arc = 1 division, illuminated by a glow-lamp, is thrown upon the mirror of the needle 3910 mm. off, and reflected on the plate 1530 mm. off; the vernier scale is 5 cm. below the other, and is reflected by a fixed mirror, placed below the first mirror. The pendulum clock has in

place of hands a silvered glass disc, 14.4 cm. diameter and 0.1 cm. thick, on which the minutes are scratched (by means of Repsold's apparatus, Zschr. Instrumk. 7. p. 396, 1887) on a circle of 12.4 cm. diameter, each minute being marked twice. Further, a second disc of 11.8 cm., 0.02 cm. thick, of silvered mica, has the even numbers on a circle of 11 cm. diameter and the odd numbers on one of 10 cm. A diaphragm allows two consecutive minutes to be printed; another diaphragm limits the visible scale to 14 divisions. Thus 31 min. 0 sec. would read $\begin{smallmatrix} 31 \\ 30 \end{smallmatrix}$;

31 min. 45 sec. $\begin{smallmatrix} 31 \\ 45 \end{smallmatrix}$ (the figures are inverted). The seconds disc

moves after every second through 6° ; this movement lasts 0.2 sec.; the disc then remains stationary for 0.8 sec. Two seconds, $\begin{smallmatrix} 27 \\ 27 \end{smallmatrix}$, might therefore appear, which would indicate that the exposures took place partly during the rest and partly during the motion of the disc. If both numbers are equally dark, the exposure, which lasts 1 sec., commenced at the 0.4th sec. of rest; if the 27 is darker, earlier. The exposure is regulated by a pendulum which closes the circuit of a glow-lamp that, burning for 1 sec. only, has no appreciable heating effect; the electric light answers better than Auer burners. The scale-lamp has a filament with two parallel branches so placed that the one illuminates the scale, the other the vernier. The silvered glass proved superior to opaque, dim, or sooted glasses. The disengaging of the pendulum and the shifting of the plate has as yet been done by hand. Plates by Weisbrod and by Sachs, and Eastman films have been used; also ordinary lenses and Zeiss' anastigmatic sets. For several magnetometers, a special time-plate would be advisable. One photograph every ten seconds would give 8640 little images in 24 hours, which would cover an area of 13.2 sq. cm. The paper contains the readings of the 150 photographs taken on July 4, 1894, between 9 h. 56 min. and 10 h. 30 min. To test the delicacy of the apparatus, a magnet is brought near. H. B.

184. *Methods for the Study of Displacement Currents in Dielectrics.* **M. de Nicolaieff.** (C. R. 119. pp. 469-471, 1894).—In the first method the author hangs the body in the form of a ring or disc by means of a bifilar between the poles of an electromagnet, the plane of the body making an angle of 45° with the axis of the magnet. When the current in the magnet alternates 930 times per minute, the deflection is 12 per cent. greater than when the current is steady. The author attributes the difference to the displacement currents in the body. In the second method a ring of the substance is hung between the poles of the electromagnet with its plane perpendicular to their axis, and one of the poles is displaced parallel to itself. The displacement currents are, as before, indicated by a difference between the deflections of the ring when the field is variable and when it is constant. J. W. C.

185. *Electrostatic Rotations in Rarefied Gases.* **R. Arnò.** (N. Cim. 36. pp. 249-251, 1894.)—The rotating electric field is produced by the method described in a former paper (Rend. Acc. Lincei, 1892, p. 284). In this field is placed an exhausted tube similar to Crookes' Radiometer, the vanes being made of thin brass. It is found that if they are made of mica they rotate whether the tube is exhausted or not, whilst metallic vanes are not acted on directly by the electric field, and do not rotate when the gas is at atmospheric pressure. If the pressure is very low the gas becomes luminous, and the vanes rotate in the same direction as the field. The author attributes the rotation to the impact of the molecules of the gas on the vanes. J. W. C.

186. *Application of Kathode Rays to the Study of Variable Magnetic Fields.* **A. Hess.** (C. R. 119. pp. 57-58, 1894.)—A Geissler tube has the end opposite the kathode closed by a metallic plate, in which is a narrow window covered with very thin aluminium. The kathode rays produced in the tube pass through the aluminium, and are received on a moving photographic plate. The apparatus is placed so that the length of the window is in the direction of the variable magnetic field to be observed. The curve on the photograph then shows the extent to which the bundle of kathode rays has been deviated at any moment, and hence the strength of the field at that moment. J. W. C.

187. *New Sensitive Idiostatic Electrometer.* **A. Righi.** (N. Cim. 36. pp. 253-259, 1894.)—Two horizontal circular metallic discs A and B have between them and parallel to them a plate C, which has the form of a narrow ring supporting two opposite sectors of 60° . Between C and the upper plate A there hangs by a bifilar suspension a light needle consisting of two opposite 60° sectors. The plates A, B, and C and the needles are placed as close together as possible, and in the equilibrium position one of the edges of the needle is over the central line of the sectors of C. The deflections are read by means of a mirror and scale. If the maximum sensitiveness is required, A and B are connected with the cover of the instrument and with earth, whilst C and the needle are connected with the body whose potential relative to the earth is required. With this arrangement the instrument constructed by Prof. Righi gave, with a potential of one volt, a deflection of 51 mm. on a scale 5 metres away. On substituting a quartz fibre for the bifilar, the deflection obtained was 400 mm. In order to measure potentials above $4\frac{1}{2}$ volts the upper disc A is connected with the case, the lower one B being connected with C and the needle. In each case the potential is proportional to the square root of the deflection. J. W. C.

188. *Temperature of the Electric Arc.* **J. Violle.** (C. R. 119. pp. 949-950, 1894.)—Violle agrees with Moissan that the temperature of the arc increases with the current. Photographs of

the positive crater show no difference when the current rises from 12 A. to 1200 A., so that this crater must be the seat of a physical phenomenon—evaporation of the carbon—which takes place at a definite temperature, as more exact measurements with currents up to 400 A. tend to prove. The spectra of the arc and of the positive carbon differ as to the distribution of the luminous intensities. Kirchhoff's law has probably to be applied with a certain reserve. One need not believe that the connection between temperature and brilliancy is the same for the spectra of gaseous and of solid bodies, and especially not when the gases are rendered luminous by the electric current, which seems capable of passing into light without heat. If, on the other hand, the arc, behaving like a conductor carrying a current, be the seat of an evolution of heat proportional to the energy spent, the temperature of the arc should rise with the current. Violle examined the temperature of the arc by means of a fine carbon pencil. Between two carbon electrodes, the proof pencil becomes hollow on the positive side and increases on the other side; the positive side behaves like a crater. Between metal electrodes, the pencil wears away in different manners—slowly between copper rods, quickly between zinc rods, where it attains a temperature considerably above the boiling-point of zinc, 930° . As the pencil is reduced to a brilliant white thread, it may be assumed that the arc has a higher temperature. Even in Geissler tubes the temperature may be high, but the mass too insignificant to show the effect. H. B.

189. *Gas Batteries with Electrodes of Compressed Spongy Metals.* **L. Cailletet** and **Collardeau**. (C. R. 119. pp. 830–834, 1894.)—The authors fill two little silk bags with about 6 gr. of spongy platinum, introduce a wire terminal of platinum into each, compress the mass strongly up to 600 atmospheres, and observe, after charging in dilute sulphuric acid, a very considerably prolonged discharge. The circuit has about 2 ohms resistance. Under ordinary atmospheric pressure, the discharge of 1.8 V. and 0.9 A. ceases within less than 10 seconds. A pressure of 15 atm. gives a polarisation-current of two minutes' duration. With higher pressures, three periods may be distinguished: the current falls almost instantaneously to 0.5 A.; then follows a minute rise of very short duration, and the current then remains constant for 16 min. with a pressure of 300 atm.; during this period 1 volt is observed; the current finally decreases, becoming zero after 32 min. (from beginning) with the pressure mentioned. Such gas accumulators would have a capacity of 56 ampère-hours per kg. of platinum under 580 atm. pressure, whilst ordinary accumulators give from 10 to 20 ampère-hours per kg. of total battery weight. Hydrogen bubbles appear before there is any liberation of oxygen. It is advisable to give the negative pole about 3 times as much metal as the positive pole. If the charge is not pushed too far and immediately followed by the discharge, 95 and even 98 per cent. of the

charge is reproduced. Joly supplied the authors with other spongy metals. Iridium behaves like platinum. Ruthenium is attacked by the diluted sulphuric acid at the positive pole, and proves inconstant. Palladium gives by far the best results. On metal foil pressure has no effect. The spongy metal (calcined cyanide) shows a constant current even below 20 atm., and the capacity of such an accumulator is more than three times as great as that of platinum cell, 176 ampère-hours per kg. of palladium. Gold proves satisfactory, but less so than platinum. Ag, Sn, Ni, Co are attacked; pressure gives no advantage. Carbon is also attacked, and evolves CO_2 . Berthelot ascribes the phenomena to the formation of hydrides and also of oxides. Platinum forms two hydrides, of which one is stable up to 200° , whilst the other dissociates even in the cold. H. B.

190. *Interference Phenomena analogous to Newton's Rings by Electric Waves along Wires.* **E. H. Barton.** (Wied. Ann. 53. pp. 513-533, 1894.)—In this work electric waves 9 m. long were generated by a Hertzian oscillator and allowed to pass along a line about 160 m. long, consisting of two parallel copper wires 1 mm. dia. spaced 8 cm. apart. A portion of the line—termed the *abnormal* part—is altered either in the character of the leads or their spacing. Von Geitler had shown that at any point where the leads were so altered, partial reflection of the waves occurred. Hence, in the present case, we may have interference between the waves reflected at the beginning and at the end of the abnormal part, whose length corresponds to the thickness of an optical “thin plate.” Thus, on gradually increasing the length of the abnormal part, the intensities of the reflected and transmitted waves exhibited *successively* periodic maxima and minima analogous to those which *simultaneously* obtain in Newton's rings. The present phenomena are more complicated than those in the optical case, owing to the rapid damping of the waves emitted by the oscillator. The subject is treated throughout both experimentally and mathematically, the two results being in fair agreement. The intensities of the waves were always measured, not detected only. For this an electrometer was used with an uncharged needle suspended by a quartz fibre and magnetically controlled. Two kinds of abnormal part were adopted. The first consisted of sheets of tin-foil 32 cm. deep, hung upon the wires at their normal spacing: the second was simply the ordinary wires, but at a distance of 0.68 cm. apart instead of the usual 8 cm. In all, ten experiments are given, including:—(1) Estimates of the damping suffered by the waves as they proceed along the line; (2) Investigations of disturbances, caused by the waves coursing to and fro along the line; and (3) Examples of abnormal parts which produce no reflection, these being made by changing to thicker wires proportionally farther apart, and *vice versa*, so as, in each case, to leave the capacity of the line unaltered. **AUTHOR.**

191. *Electric Oscillations of Short Wave-length producing Phenomena analogous to the principal Phenomena of Optics.* **A. Righi.** (R. Accad. d. Scienze dell' Istituto di Bologna, 4. pp. 487-590, 1894.)—Previous experimenters used waves down to 66 cm. long. These necessitated cumbrous apparatus to avoid diffraction effects. Waves down to 2.6 cm. long are here employed, thus affording a very close analogy between the corresponding electric and luminous phenomena. The oscillator consists of two spheres, between which the sparks pass through oil. It is charged by a Holtz machine capable of giving sparks about 30 cm. long. The resonator consists of a piece of glass, silvered for part of its length, the silver coating being the resonator proper, a fine scratch, about 0.002 mm. wide, across its middle acting as spark-gap. The sparks are observed with a lens. Both oscillator and resonator are fixed along the focal lines of parabolic cylindrical mirrors, which are capable of rotation and are provided with graduated circles. The spheres of the oscillator most frequently used are 3.75 cm. dia., and are placed almost in contact. The corresponding resonator was 4 cm. long and 0.2 cm. wide, the wave-length being 10.6 cm. Other apparatus for waves of 2.6 cm. and 20 cm. are occasionally adopted, the latter being convenient for lecture demonstration and for diffraction effects. A circular resonator is also used, consisting of an annular silver-coating on glass, the spark-gap being a radial scratch. The chief experiments performed fall under the following heads:—Repetition of the classical experiments of Hertz; the Study of Interference Bands, (i) from Fresnel's Mirrors, (ii) with a Single Mirror, and (iii) with a Biprism of Sulphur; Determinations of Wave-Lengths and Refractive Indices; Interference Phenomena (by Reflection and Transmission) with Thin Plates of Paraffin and Sulphur; Diffraction through a Slit and at the edge of an "opaque" body; Reflection from Dielectrics; Metallic Reflection; Elliptically and Circularly Polarised Waves by Reflection from Dielectrics, one method for circular polarisation involving three total internal reflections in a paraffin prism analogous to the parallelepiped of Fresnel; Experiments with Prisms, Parallel Plates, and Lenses; Polarisation by Reflection from a "Pile of Plates"; Imitation of Luminous Fountain, electric waves entering at one end of a curved piece of paraffin emerging at the other by repeated total internal reflections; Diminution of the Intensity of Radiation caused by the Interposition of Plates of various Dielectrics [the results here obtained depend in part upon the multiple reflections occurring between the two faces of the plate and not upon the absorption alone]. The author has not yet been able to obtain with Electric Waves any phenomena analogous to the Rotatory Polarisation of Light nor to Double Refraction, unless some results produced by wood may be so regarded. Again, in the search for phenomena with electrical waves analogous to Electro-optical and to Magneto-optical phenomena, only negative, or at most uncertain, results have been obtained. E. H. B.

CHEMICAL PHYSICS.

192. *Lowering of Freezing-Point of Solvent.* **H. C. Jones.** (Wied. Ann. 53. pp. 392-395, 1894.)—This is a defence against F. Kohlrausch's criticism (Wied. Ann. 51. p. 524) of his results (Phil. Mag. (5) 36. p. 465) which differ, sometimes widely, from those obtained by Loomis (Wied. Ann. 51. p. 500); he upholds his own temperature-estimations and ascribes the differences to impurity in the substances used by Loomis, more especially as in the case of phosphoric acid his own results differ by but 4 p. cent. from some given by Arrhenius, from which those of Loomis differ by 24 p. cent. Further, the percentages of dissociation calculated from his experiments are much nearer those deduced from Kohlrausch's experiments on Conductivity than are those obtained from Loomis' results. R. E. B.

193. *Refraction and Density of Dilute Solutions.* **W. Hallwachs.** (Wied. Ann. 53. pp. 1-13, 1894.)—The refractive powers calculated from the formulæ $n-1/d$ and $n^2-1/(n^2+2)d$ in the case of acetic, tartaric, hydrochloric, and sulphuric acids, cane-sugar, NaCl, MgSO₄, ZnSO₄, Na₂CO₃, CuSO₄ in dilute solutions are compared with the ionisation for similar solutions. The refractive powers are found to be very constant for the range of solutions examined; and it is concluded that the dissociation exercises no detectable influence on the index of refraction. S. S.

194. *Density of Dilute Solutions.* **F. Kohlrausch and W. Hallwachs.** (Wied. Ann. 53. pp. 14-42, 1894.)—Details are given of a very careful determination of the density of very dilute solutions by a method of weighing an immersed body. The solutions contained NaCl, Na₂CO₃, MgSO₄, ZnSO₄, HCl, H₂SO₄, H₃PO₄, tartaric, monochloracetic and acetic acids, and sugar. The results are considered in connection with similar determinations for strong solutions, and a table is given showing the molecular increase of density for these solutions; *i. e.* the value of $S-1/m$, where S is the density of the solution and m the gram-equivalents in a litre. A second table gives the volume in c.cm. of a gram-equivalent of the substances in solution; and it is found that they form two classes: (*a*) containing H₂SO₄, H₃PO₄, MgSO₄, ZnSO₄, and tartaric and monochloracetic acids; for these substances the curve expressing this volume bends sharply downwards at great dilutions; and (*b*) containing NaCl, Na₂CO₃, HCl, sugar, and acetic acid, for which the curve is a straight line. S. S.

195. *Solutions.* **G. Charpy.** (C. R. 119. pp. 156-158, 1894.)—By plotting curves representing the density of a saline solution as a function of the molecular concentration, the author shows

that if the molecular weight of liquid water at 0° be taken as 3×18 , the density of a saline solution increases proportionally to the molecular concentration. He further shows that the densities of solutions of similar salts of equal concentration are very nearly proportional to their molecular weights. S. R.

196. *Dissociation Theory of Solutions.* **A. Schlamp.** (Zschr. phys. Chem. 14. pp. 272–285.)—In aqueous solution the amount of dissociation of a salt, calculated from the lowering of the freezing-point or the raising of the boiling-point, agrees with the amount deduced from measurements of the electrical conductivity. The author examines the question whether this holds good

for other solvents. For propyl alcohol, the formula $\frac{0.02 T^2}{W}$ for the molecular raising of the boiling-point gives a value 16.88—the value of W , the latent heat of the vapour, being found to be 162.6 cal., and the boiling-point T , 97.32° . Experiments on solutions of salicylic acid in propyl alcohol gave 17.34, showing a ratio of the formula weight to the molecular weight of 1.05. The following table gives the corresponding ratios for other bodies in column 3, and the same ratio calculated from the electrical conductivities in column 4. The latter is calculated from the formula $i = 1 + \alpha(k - 1)$, where α is the amount of dissociation, equal to the ratio of the actual molecular conductivity to its limiting value at infinite dilution, and k the number of ions into which each molecule can be dissociated.

Substance dissolved in Propyl Alcohol.	Normal.	i from boiling- points.	i from con- ductivities.
Lithium Chloride	$\frac{1}{3.6}$	1.18	1.44
Sodium Iodide	$\frac{1}{6}$	1.04	1.34
Calcium Chloride	$\frac{1}{5.1}$..	1.33
Lithium Salicylate	$\frac{1}{8}$	0.55	1.17
Salicylic Acid	$\frac{1}{6}$	1.05	1.00

The following limiting values for the molecular conductivity at 15.2° in propyl alcohol are the mean of those found graphically, and from the formula $\mu = \mu_\infty - bm$, where μ denotes the molecular conductivity, m the number of molecules, and b a constant.

	Water.	Ethyl Alcohol.	Propyl Alcohol.
Lithium Chloride ..	911	293	134
Sodium Iodide	966	360	189
Calcium Chloride ..	1030	157.5	82
Lithium Salicylate..	568	..	105

The ratio of μ_∞ in water to μ_∞ in propyl alcohol lies between 6 and 7, except for calcium chloride, which gives a nearly double value 12.6. The ratio of μ_∞ in ethyl and propyl alcohols is nearly 2, which is almost the same as the inverse ratio of their viscosities.

W. C. D. W.

197. *Hydrolysis of the Salts of Weak Acids and Weak Bases.* **S. Arrhenius.** (Zschr. phys. Chem. 13. pp. 407-411, 1894.)—Lellmann and Schliemann obtained results which did not appear to be in accordance with the dissociation theory. In this paper the extinction coefficients of solutions of helianthin in various solvents are calculated from the theory, and shown to agree in most cases with the observed values. W. C. D. W.

198. *Absorption-Coefficient of CO_2 and H_2S in Water at Freezing-point.* **K. Prytz** and **H. Holst.** (Wied. Ann. 54. pp. 130-138, 1895).—A careful determination by a method different from Bunsen's gives $1.7308 \pm .0014$ and $4.6796 \pm .0082$ for these coefficients at 0° , which are respectively 3.8 per cent. less and 6.6 per cent. greater than those given by Bunsen. Substituted in Prytz' theoretically deduced expression for the lowering of the freezing-point of water by absorption of gas, they give results not differing greatly from those observed, but still indicate that the H_2S used was not pure. R. E. B.

199. *Superficial Tension of Polarised Mercury.* **O. Wiedenburg.** (Wied. Ann. 54. pp. 64-84, 1895.)—This contains the application of the author's theory (Abstract 90) to the polarisation and superficial tension of mercury electrodes. The experimental results of Paschen and Meyer are used for comparison, and are found to be in excellent agreement with the theory. Finally, the theory is used to furnish an estimate of the size of a molecule. S. S.

200. *Temperature-Coefficients for Ethereal Salts.* **A. Bartoli.** (Nuov. Cim. 36. pp. 57-70, 1894.)—The author extends his work on the conductivity of organic substances to ethereal salts. He uses an arbitrary unit, and finds (1) that the conductivity at all ordinary temperatures, and also at the respective boiling-points, decreases with increase of molecular weight; (2) that the temperature-coefficient is positive, the increment per degree being greater for salts of large molecular weight than for those with small molecular weight; (3) that ethyl acetate is anomalous, its conductivity decreasing with increase of temperature; and (4) that the addition of 1 to 20 per cent. of an alcohol causes the solution to have a negative temperature-coefficient. S. S.

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